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METHODS OF GAS ANALYSIS

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METHODS OF GAS ANALYSIS

BY

DR. WALTHER HEMPEL

PROFESSOR OF CHEMISTRY IN THE DRESDEN *TECHNISCHE HOCHSCHULE*

TRANSLATED FROM THE THIRD GERMAN EDITION AND CONSIDERABLY ENLARGED

BY

L. M. DENNIS

PROFESSOR OF ANALYTICAL AND INORGANIC CHEMISTRY IN CORNELL UNIVERSITY

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PREFACE TO THE SECOND GERMAN EDITION

In publishing my "New Methods for the Analysis of Gases," it was not my intention to write a manual of gas analysis, but merely to describe my own researches and the construction of apparatus. My present plan, however, after ten years' experience and the most varied work with gases and their analysis, is to describe all of the operations which are involved in the analysis of gases with my apparatus. I have thought to give the book especial value by limiting myself to the description of those methods which, in my opinion, are at the present time the most practical. I have not endeavoured to give a complete description of all known methods, because the book would then become too bulky to be used as the laboratory guide which it is intended to be.

The apparatus devised by Pettersson has been described, because a wholly new principle in the measurement of gases is there brought into use. In the following pages I hope to give a guide to gas analysis by the help of which the various examinations, even the most difficult, can be carried out.

WALTHER HEMPEL.

DRESDEN,
December, 1889.

PREFACE TO THE TRANSLATION OF THE SECOND GERMAN EDITION

THE rapidly growing recognition of the importance of gas analysis in the field of industrial as well as of pure chemistry, has made it seem probable that a translation of the latest work of so eminent an investigator in this line as Professor Hempel might prove acceptable to English-reading chemists. While preparing this English edition, the Translator was so fortunate as to enjoy throughout the progress of the work the personal coöperation of the author, and the changes that have been made were either suggested by Professor Hempel himself, or inserted with his approval. The chapter upon the determination of the heating-power of fuel has been largely rewritten, and new cuts of the latest forms of apparatus have been introduced in the place of those in the German edition. The chapter upon the analysis of illuminating gas has also been somewhat changed, and a new method for the determination of the hydrocarbon vapours inserted. The other and less important alterations have been made in the desire to incorporate so far as possible the researches that have appeared since the publication of the German edition.

L. M. DENNIS.

ITHACA, NEW YORK,
November, 1891.

PREFACE TO THE THIRD GERMAN EDITION

MANY important investigations in the field of gas analysis have been published in the interval that has elapsed since the appearance of the second edition of this work, and it is with the idea of bringing together these and his own experimental researches that the author has been led to prepare this third edition.

The division into technical and exact gas analysis has been abandoned because, on the one hand, apparatus originally intended for technical purposes may advantageously be employed for many purely scientific investigations, and, on the other hand, technical analyses must often satisfy the most exacting demands as to accuracy.

DR. WALTHER HEMPEL.

DRESDEN,
November, 1899.

PREFACE TO THE TRANSLATION OF THE THIRD GERMAN EDITION

IN this translation of the third German edition of Professor Hempel's "Methods of Gas Analysis," the work has been thoroughly revised by both the author and the Translator, and has been changed to such an extent that this translation may indeed be regarded as a fourth edition of the book.

The determination of atmospheric oxygen by Kreusler's method has been omitted. The additions comprise several new methods of collecting and keeping gas samples; determinations with the Honigmann, Bunte, and Orsat apparatus; the new Hempel methods for exact gas analysis; new methods for the determination of combustible gases; the separation of argon from the atmosphere; improved methods for the determination of carbon monoxide in gas mixtures; the analysis of acetylene gas; the examination of gases produced by living bacteria; the simultaneous determination of fluorine and carbon dioxide; the determination of the heating power of gases; sulphur in organic substances; the gas lantern; the volumetric determination of carbon in iron; the analysis of gases evolved in the electrolysis of chlorides and in the manufacture of bleaching powder, together with many minor changes and additions throughout the book.

L. M. DENNIS.

ITHACA, NEW YORK,
March, 1902.

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PART I

GENERAL METHODS

CHAPTER I

THE COLLECTING AND KEEPING OF GASES

In gas analysis, as in all other analytical work, the proper taking of the sample is one of the most important operations. Notwithstanding the rapid movement of gas molecules, currents of gases are often of varying composition, especially when chemical processes are simultaneously going on. On this account the place at which the samples of gas are taken is of the greatest significance. In pipes or other channels the point of smallest cross-section is the most suitable. In the examination of furnace gases it is best to take the sample at the point where the visible flame ends, because farther away, on account of the porosity of the wall, considerable quantities of air are always mixed with the gases from the fire. To take the sample, an iron tube is introduced into the furnace at a suitable point. A small lead pipe, such as is used for pneumatic bells, is attached to the outer end of the iron tube by means of a piece of rubber tubing. At temperatures under 300° the lead pipe itself may be inserted into the furnace. The great advantage possessed by such lead pipe is that it is very small internally and can be manipulated as easily as rubber tubing. For very high temperatures either porcelain tubes or cooled iron tubes may be used. With acid gases glass tubes should be employed if possible.

Long rubber tubes must be avoided, but short pieces may safely be used for connections. Rubber receivers also are to be rejected. Vulcanised rubber acts toward gases as does a liquid, absorbing the gases, and later, according to the prevailing pressure, giving them up again. For example, a piece of rubber tubing, 3 cm. long and from 4 to 5 mm. external diameter, absorbed 0.2 ccm. of carbon dioxide and 0.9 ccm. of nitrous oxide, and on lying in the air it gradually gave up these gases.

A rubber balloon of about 150 ccm. capacity, which was filled with nitrogen wholly free from oxygen, contained after one hour 1 per cent of oxygen, and after six and one-half hours 4½ per cent of oxygen. The experiments of Harbeck and Lunge show that even very thick rubber connections allow small quantities of gases to pass through the walls.[1] These authors state that rubber is made much more impervious to the passage of gases by coating it with copal varnish.

If the place where the gases are to be collected is directly accessible, as, for example, in the examination of mine gases, the small "medicine bottles"[2] proposed by Bunsen may be used, the neck of the bottle being drawn out in the flame of the blast-lamp as in Fig. 1. Bunsen states[3] that the bottle should first be carefully heated between the shoulder and the neck, and the neck then drawn out by means of suitable tongs (Fig. 2). To fill the bottle with gas, the air in the bottle is sucked out through a small glass tube reaching to the bottom, this operation being repeated until the air originally in the bottle is completely replaced by gas from outside. Five or six full breaths are sufficient. It is self-evident that at each exhalation of the air sucked from the bottle, one must step aside from the spot where the gas sample is being taken. The tightly stoppered bottle is then slightly warmed over a spirit lamp, and equilibrium between the expanding air inside the bottle and the outside atmosphere is reëstablished by lifting the cork for a moment. After cooling, the diminished pressure inside the bottle prevents the blowing-out of the glass when the narrow neck is fused together. The fusion may conveniently be performed with the blow-pipe shown in Fig. 3. The small

---

[1] *Zeitschr. f. anorganische Chemie*, **16**, 30.

[2] These so-called medicine bottles are common glass bottles about 12 cm. high. They were recommended by Bunsen because they can be found almost everywhere, even small village drug stores having a supply of them.

[3] Bunsen, *Gasometrische Methoden*, 2d ed. p. 12.

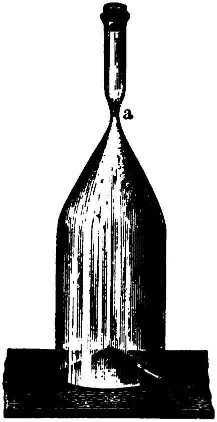

FIG 1.

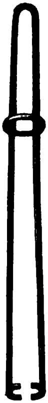

FIG. 2.

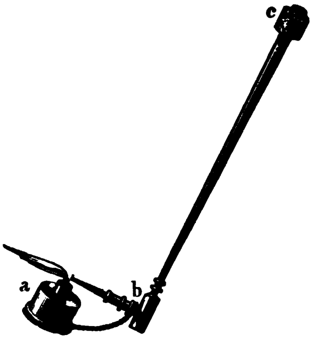

FIG. 3.

lamp *a* holds about 3 g. of oil, and is connected with the blow-pipe by means of a flexible wire that carries a collar *b* through which the tip of the blow-pipe is inserted.

The cork *c* serves as a mouth-piece by means of which the whole apparatus can be held and guided by the teeth alone. Thus both hands are left free, and the flame can still be moved in all directions, since the relative positions of the blow-pipe tip and the lamp remain the same, however the instrument be held.

In actual practice, however, it has been found difficult to draw out the neck of a bottle without cracking it, and therefore these small sampling tubes had best be made in the laboratory from easily fusible glass tubing.

The arrangement used by the author in his researches "upon the composition of the atmosphere at different parts of the earth" is also a very convenient one. The air was collected in glass tubes of the form shown in Fig. 4. *d* is about 4 mm. thick; *a*, *b*, and *c*, only 1 mm. These tubes were heated in an air-bath in the laboratory to 200°, and were then exhausted with the mercury air-pump and fused together at *c*. By simply breaking the tube at *b*, it fills instantly and completely with the air in question. The tubes are then closed for a few moments with a rubber cap, and are melted together at *a* over a candle. The exhausting with the air-pump has the advantage of rendering one less dependent upon the care of the

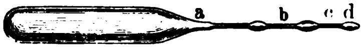

FIG. 4.

person who fills the tubes. If, however, it is desired to avoid this exhausting, the tubes are given the following form (Fig. 5 *a*). To fill such a tube, the gas to be examined is drawn through it and the tube is then fused together at *a* and *b* in a candle flame (Fig. 5 *b*).

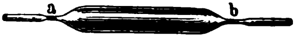

FIG. 5 *a*.

Such tubes can be most safely shipped by packing them in sawdust in boxes which have a separate compartment for each tube. The boxes themselves are placed in a larger box filled with hay.

The tube last described is filled by the displacement of the air already contained therein. Naturally it is here presupposed that large amounts of gas are at one's disposal. If only a small quantity of gas is obtainable, the receiver must be filled with water or mercury, which is then displaced by the gas. If it is possible to analyse the gas samples within a short time after their collection, we may employ small glass tubes of the form shown in Fig. 6. Such tubes may conveniently be used for the examination of the air in coal mines. Water can be used only when it is first saturated with the gases in question,

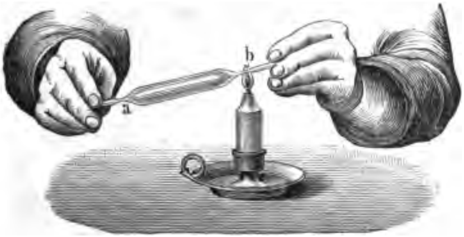

FIG. 5 *b*.

as, for example, is always the case with the water of bubbling springs.

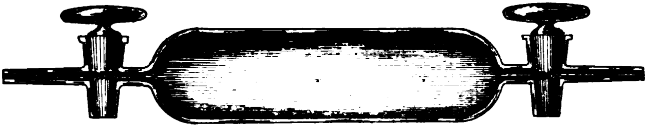

FIG. 6.

To collect gas from such springs as are directly accessible, the small apparatus proposed by Bunsen[1] is used (Fig. 7).

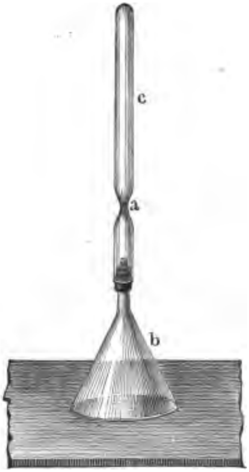

FIG. 7.

This consists of a test-tube *c* of from 40 to 60 ccm. capacity, drawn out at *a* before the blast-lamp to the size of a fine straw, and connected air-tight with the funnel *b* by means of a well-fitting cork or a piece of vulcanised rubber tubing. Instead of the test-tube a small long-necked medicine bottle may be used, this being drawn out in the middle of the neck to a similar strawlike contraction. The apparatus is then filled with the water of the spring. This cannot be done without access of air, which would change the composition of the gases diffused through the spring water in the tube. Hence the inverted apparatus, with the mouth of the funnel upward, is lowered below the level of the spring, and, with a narrow tube reaching to the bottom of the test-tube, the water which in the first filling had come in contact with the air is sucked out until one is satisfied that it has been entirely replaced by other water from the spring. If now the gas of the spring is allowed to rise through the funnel into the test-tube thus filled, the purity of the sample is assured. If the rising bubbles stop in the neck of the funnel or at the contraction *a*, they can easily be made to ascend by tapping the edge of the funnel upon some hard substance. The apparatus is then placed in a small dish and removed from the spring, and the tube is melted together at *a*. This can easily be done with the blow-pipe, the moisture at the point *a* having first been driven away by warming.

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[1] Bunsen, *Gasometrische Methoden*, 2d ed. p. 2.

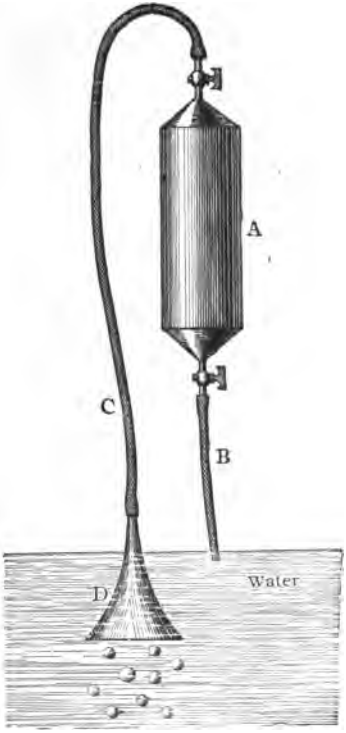

FIG. 8.

W. Ramsay and M. W. Travers have proposed the apparatus shown in Fig. 8 for collecting large quantities of gases from mineral waters. The cylinder *A* is filled with the water of the spring, and the rising bubbles of gas pass into the cylinder through the funnel *D* and the tube *C*.

For the determination of the volume and composition of the absorbed gases in liquids, the Tiemann and Preusse modification of Reichardt's apparatus[1] can be recommended (Fig. 9).

This consists of two flasks *A* and *B*, each of about 1 liter capacity, and connected by tubes with the gas-collector *C*. The flask *A* is fitted with a perforated rubber stopper in which is inserted the glass tube *a* bent at a right angle and ending flush with the lower surface of the stopper. *a* is joined by a piece of rubber tubing to the tube *bc*, which in turn connects with the gas-collector *C*. *C* is held by a clamp, has a diameter of 35 mm., is about 300 mm.

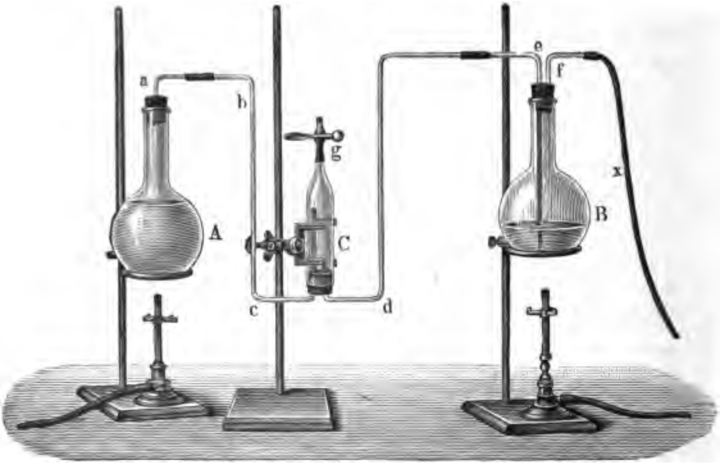

Fig. 9.

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1879, p. 1768.

long, and at the upper end is drawn out to a short, narrow, and slightly bent tube which can be closed with the rubber tube and pinchcock *g*. In the lower end of *C* is a rubber stopper with two holes through one of which the tube *bc*, projecting about 80 mm. into *C*, is inserted. Through the other opening passes the tube *d* which extends only slightly beyond the stopper and connects *C* with the flask *B*. *B* has a double-bore rubber stopper carrying the tubes *e* and *f*. *e* ends about 10 mm. above the bottom of the flask, and above the stopper it is bent at a right angle and is connected with *d*. The tube *f*, which need not project below the stopper, carries a thin rubber tube *x* about 1 m. in length and provided with a mouthpiece. A pinchcock for closing the rubber tube between *a* and *b* is also needed.

The apparatus thus arranged is made ready for a determination by filling the flask *B* somewhat more than half full of boiled water and removing the flask *A* by slipping the tube *a* out of the rubber connection; then, by blowing into the rubber tube *x*, water is driven over from the flask *B* into the gas-collector *C* and the adjoining tubes, until the air is wholly displaced. The rubber tubes at *b* and *g* are now closed with pinchcocks. The flask *A* is then filled to the brim with distilled water, the stopper is inserted, water being thereby driven into the tube *a*, and the flask is again connected with *b*, the pinchcock being opened.

The water in *B* is now heated to gentle boiling, and that in *A* is allowed to boil somewhat more rapidly. The absorbed air is thus driven out, and the gases which are dissolved in the water in *A* and *C* collect in the upper part of *C*, from which they are removed by occasionally opening the pinchcock at *g* and blowing into the rubber tube *x*.

When, upon cooling the apparatus, the gases which have collected disappear, the heating of the flask *A* is discontinued, the pinchcock between *a* and *b* is closed, and *A* is disconnected and emptied. The water in *C* and *B* is now entirely free from absorbed gases, and air cannot enter from without because the liquid in *B* is kept continually boiling. The apparatus is now ready for a determination, which is made as follows: —

The cooled flask *A*, whose capacity has been previously determined, is filled with the water to be examined, and the stopper is pressed in so far that the air in the tube *a* is completely driven out. *a* is then connected with *b*, care being taken that in so doing no air-bubbles are enclosed. The pinchcock between *a* and *b* is opened, and the water in *A* is heated to gentle boiling The dissolved gases are hereby driven over into the gas-collector *C*. Steam is formed at the same time. The heating of the flask *A* must now be so regulated that the gas and steam evolved never drive out more than half the liquid in *C*: otherwise there is danger of gas-bubbles entering the tubes *d* and *e* and thus escaping.

After heating for about twenty minutes, the flame under *A* is removed. In a few minutes the steam in *A* and *C* condenses, and water passes from *B* toward *C* and *A*. If a gas-bubble is observed in *A*, the flask *A* must again be heated and cooled in the manner just described. The operation is ended when the hot liquid flows back and completely fills *A*. The rubber tube *g* is then connected with a small tube which is filled with water or mercury, and the gas standing over the hot liquid in *C* is driven over into a eudiometer, gas burette, or gasometer by blowing into the tube *x* and opening the pinchcock *g*.

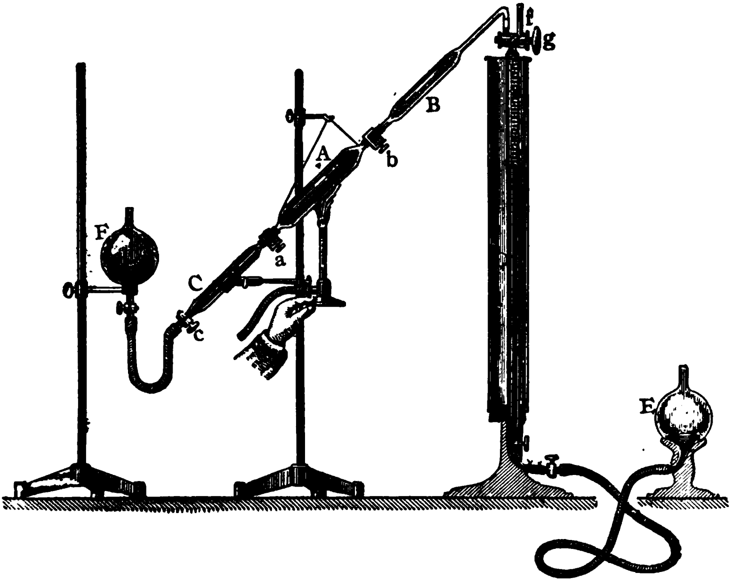

FIG. 10.

F. Hoppe-Seyler[1] has devised a somewhat more complicated apparatus for extracting the absorbed gases from the waters of springs and rivers. It is a modification of the method proposed by Bunsen and Dittmar. The apparatus shown in Fig. 10 varies slightly from that suggested by Hoppe-Seyler in that a gas burette *D* (see page 35) is used as the collecting vessel and air-pump. Any other burette with a two-way stopcock may, of course, be employed in place of the burette here figured. The apparatus consists of the gas burette *D* filled with mercury, the glass tubes *A*, *B*, and *C* and the level-bulb *F*. The tubes *A*, *B*, and *C* are joined together with pieces of rubber tubing. Screw pinchcocks are placed at *a* and *b*. To extract the dissolved gases from a sample of water, a bent glass tube is inserted at *b* and the tubes *A* and *C* are filled with mercury by raising the level-bulb *F*, the mercury being allowed to rise until it reaches the tube which has been inserted at *b*. The glass tube is then introduced into the vessel which contains the water to be examined, and by lowering the level-bulb *F* water is drawn into the apparatus until the tube *A* is completely filled with it. The bent tube is then removed from *b*, *B* is inserted in its place, and the pinchcock at *b* is closed. The two-way stopcock of the burette is now turned so that the burette communicates with the exit tube *f*. The air in the burette is driven out by raising the level-bulb *E*, and the stopcock *g* is then turned so that the burette communicates with the tube *B*. Upon lowering the level-bulb as far as possible the burette may now be made to function as a mercury air-pump and the air which is in *B* can be drawn over into *D*. Upon closing the stopcock *g*, raising the bulb *E*, and then turning *G* so that the burette communicates with *f*, the air which has been drawn out of *B* may be expelled from the burette. This operation is then repeated until no more bubbles of gas appear. When the tube *B* has thus been exhausted of air, the cocks *a*, *b*, and *c* are opened, and the water in the apparatus is brought to boiling by heating the tubes *A* and *C* directly with the Bunsen burner. The escape of the gas into the vacuum of *B* begins at once. After about five minutes, the water in *A* is brought nearly to the height of the pinchcock *b* by raising or lowering the level-bulb *F*. *b* is then closed and the gas in *B* is pumped out by raising and lowering the level-bulb *E* in the manner above described. *f* is connected by means of a bent capillary tube with a second gas burette or gas pipette, and the gas which has been drawn over into *D* from *B* is transferred to the second gas holder by turning *g* so that *D* communicates with *f*. The pinchcock *b* is then opened, the water in *A* is again brought to boiling, and the gas set free by this second treatment is added to the portion first obtained. By repeating the process three times it is easily possible to completely extract all of the absorbed gases with the exception of carbon dioxide. This latter gas is so persistently retained by the water that according to the experiments of Jacobsen it is impossible to entirely remove it. Pettersson has shown that even after strongly acidifying the water with sulphuric acid the carbon dioxide cannot be completely driven out by boiling.

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[1] *Zeitschr. f. analyt. Chem.* **31**, 367.

Gases are set free in many chemical reactions that take place in sealed tubes. If one wishes to examine these gases, Bunsen directs[1] that when the tube is fused together, it be drawn out to a fine tip about 2 mm. wide and 50 mm. long. To collect the gases given off, a mark is made at *a* with a sharp file, and the tip is connected with a capillary glass tube by means of a short piece of rubber tubing (Fig. 11).

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[1] Bunsen, *Gasometrische Methoden*, 2d ed. p. 10.

For safety's sake wire ligatures are put on at *b* and *c*. On breaking the tube inside the rubber at *a*, the gas passes through the delivery tube and can be collected in any desired receiver. If very strong pressure in the tube is to be expected, the rubber connection is surrounded with a strip of linen, and the tube itself is wrapped in a cloth. A third ligature put on at *d* makes it possible to stop the escape of gas at any time, the rubber forming with the broken-off glass tube a Bunsen rubber stopcock.

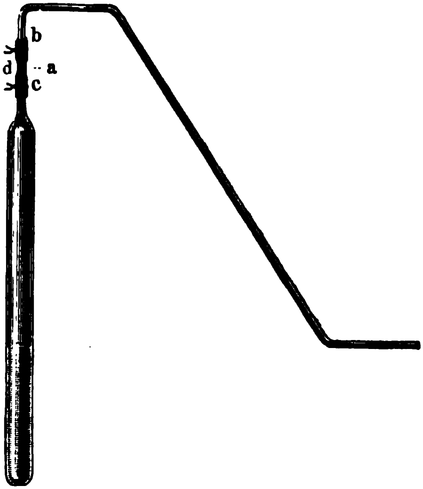

FIG. 11.

To extract the gases which may be present in minerals or stones, Ramsay and Travers recommend that the mineral be first reduced to a fine powder and be then mixed with double its weight of primary potassium sulphate. The mixture is placed in a hard-glass tube which is connected with an air-pump. After the tube has been exhausted it is heated to redness with a large Bunsen burner. The escaping gases are pumped out and are collected in a small tube which contains some potassium hydroxide. In order to exclude the possibility of leakage, the tube is joined to the air-pump in the manner shown in Fig. 12. As may be seen from the drawing, the large tube is drawn out at *A*, a piece of rubber tubing is placed over the end of the small tube *B*, and after it has been inserted in the contraction at *A*, the joint is covered with mercury standing in the wide portion *C*. In most cases the gases which are present in the mineral are driven out by heating the substance alone without the addition of primary potassium sulphate.

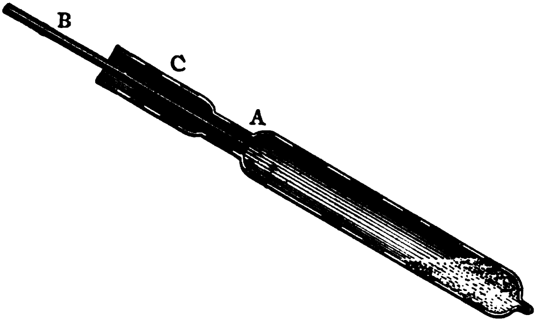

FIG. 12.

If one wishes to extract only those gases which are mechanically enclosed in a mineral or metal, the problem becomes much more difficult, since chemical changes in the substance may easily occur when it is heated. Thus carbonates will lose carbon dioxide, while ferrous salts are able to reduce carbon dioxide to carbon monoxide and water vapour to hydrogen. The procedure devised by the author to meet such cases is as follows: A large piece, *B*, of the mineral or metal in question is placed in a cylinder *A* (Fig. 13) made of heavy sheet iron and the space between the sample and the cylinder is filled with plaster of Paris. Mercury is then poured on the top of the sample until it is covered with a layer about 4 cm. thick. By means of a hollow steel drill, closed at the top and filled with mercury, a hole of desirable depth is bored in the top of the sample, the drill being driven in by means of a hammer and being frequently slightly raised and turned during the procedure. Its lower end must, of course, never be raised above the level of the mercury. The powder from the drilling, together with the gases in the sample, collect inside the steel drill and are removed from the latter in the manner described below.

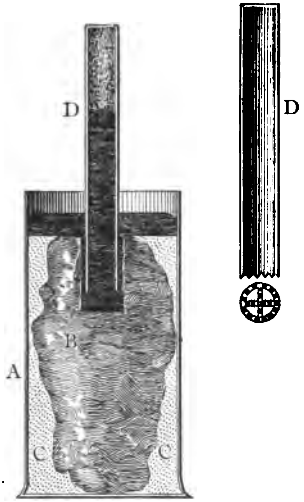

Fig. 18.

The drill may best be made by boring out a solid bar of steel and the lower edge is then notched. In order to pulverise the particles of the sample as finely as possible during the drilling, a notched cross-piece is inserted into the open end of the drill tube. To fill the drill with mercury, it is placed open end up and a straight glass adapter is pushed over the open end of the drill and fastened in place by a rubber ring. The drill and adapter are then completely filled with mercury, the open end is closed with the finger, and the tube is inverted in a deep vessel filled with mercury. The adapter and rubber ring are then slipped off, a shallow dish is brought under the end of the drill, and the latter is then transferred to the cylinder *A*, the dish being removed after the mouth of the drill has been brought under the mercury in *A*. In this manner it is easy to completely fill the drill with mercury. The layer of gas which persistently adheres to all larger surfaces is not removed from the drill when the latter is filled with mercury, and for this reason a small quantity of air is always present in the gases which have been set free from the mineral during the drilling. In order to eliminate this error in the analysis two determinations must always be made. In the first, the amount of carbon dioxide in the gas mixture is accurately determined. The small amount of this constituent which is present in the air can be disregarded when dealing with such small quantities of gas as are here in question. In the second experiment, carbon dioxide is passed into the drill and into the apparatus (see below) that is designed to receive the gases from the drill, until the layer of gas first adhering to the surface has been completely driven out by the carbon dioxide, and all air has thus been expelled. In carrying out this operation, the author always uses a cylinder charged with liquid carbon dioxide because this is much purer than that which is evolved by the action of acid upon marble. Ordinary marble is so porous that appreciable quantities of air are always set free with carbon dioxide when it is treated with an acid.

To now remove both the gases which have collected, as well as the powdered mineral in the hollow drill, a shallow dish is slipped under the mouth of the drill, the latter is lifted from the cylinder *A*, the dish is placed upon the ring of an ordinary iron stand, and the drill is fastened in a clamp so that it stands in a perpendicular position. The outside of the drill is now washed with a stream of water to remove any powdered mineral adhering to it, for the presence of this powder might prevent a gas-tight joint between the outer surface of the drill and the rubber ring which is to be slipped over it. The drill and dish are then placed in a deep vessel filled with mercury, the dish is removed, and a rubber ring is slipped over the lower end of the drill. A glass adapter is then pushed on to the rubber ring, the operation, of course, being carried on under the level of the mercury. In the meantime, the apparatus into which the gas is to be drawn off (Fig. 14) has been filled with mercury to such a height that the inverted half-bottle *E* is completely filled. A rubber band is now slipped over the lower, narrow end of the adapter *J*. This end is then closed with the finger, and drill and adapter are transferred to the mercury contained in the bottle *E*, the end of

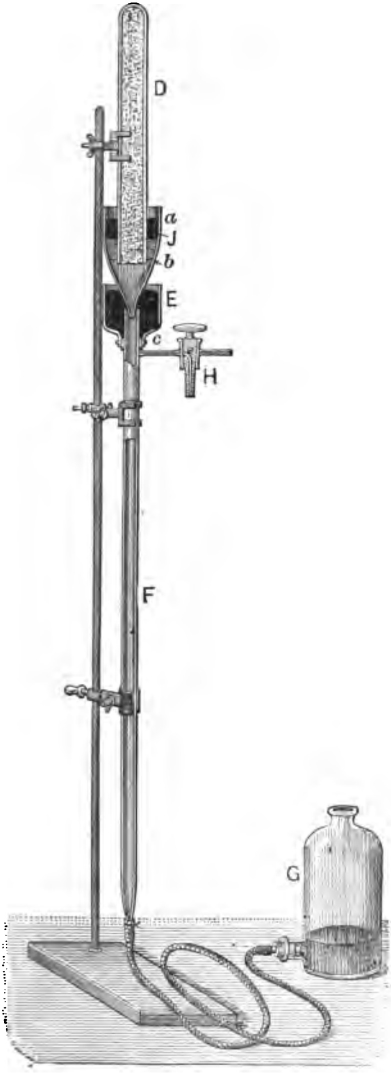

Fig. 14.

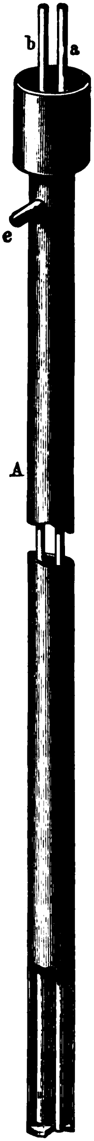

Fig. 15.

the adapter being inserted in the upper end of the tube *F*. The drill is now fastened firmly in position by means of the clamp, and upon lowering the level-bulb *G* the inside of the drill is brought under diminished pressure. The positions of the various parts of the apparatus at this point are shown in Fig. 14. The rubber rings at *b* and *c* are rendered completely gas-tight by the mercury which stands over them. Upon connecting the stopcock *H* with the mercury air-pump, the gases which have collected in *D* may now easily be removed and transferred to another vessel for analysis.

The taking of the gas sample is especially difficult when at the same time the disturbing influences of elevated temperature, chemical action, and high mechanical pressure must be overcome, as for example in the collecting of gases from the blast-furnace. Bunsen and Playfair, in their investigation at the blast-furnace in Alfreton, England, introduced a wrought-iron tube into the throat of the furnace and allowed it to sink with the charge. The tube consisted of five pieces, which were screwed on from time to time as the tube sank.

Winkler has proposed[1] the device shown in Fig. 15, the form here given being that used by Schertel in his investigations on the Freiberg lead furnaces. They both used three tubes, which could be lengthened as much as desired by screwing on additional pieces. The bottom of the outer tube is welded on, and into it the two inner tubes are tightly screwed; *b* has a number of side openings just above its lower

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[1] Clemens Winkler, *Anleitung zur chemischen Untersuchung der Industrie-Gase*, Part II, p. 7.

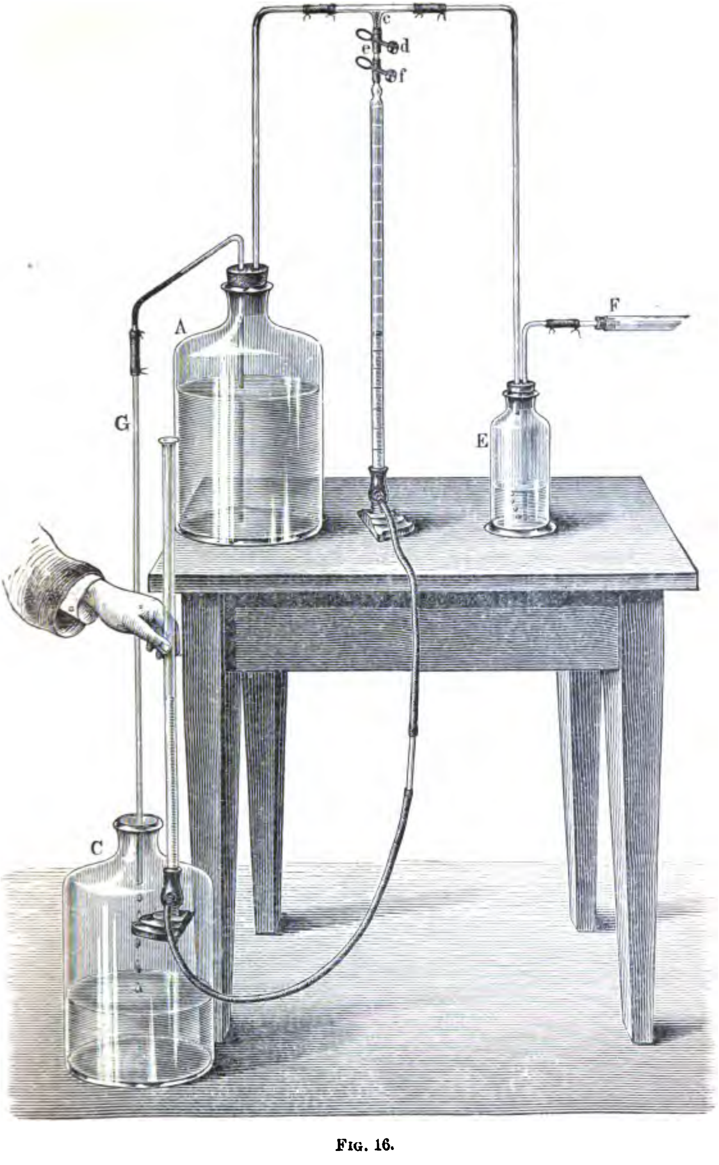
c
e
d
e
f
A
F
G
E
C

FIG. 16.

end, but it does not pass through the bottom, whereas *a* does. When in use, a stream of water enters at *b* and, passing into *A*, surrounds the tube *a* and protects it from the action of the heat. The water is led off at *c* by a rubber tube. The stoppage of the tube by dust is prevented by putting a wad of asbestos into the mouth of the tube *a* while the apparatus is being introduced into the furnace. The tube is let down by a pulley to the lowest point at which the gas is to be taken. The asbestos stopper is then pushed out with a stiff iron wire. To take samples of gas from points higher up, the tube is simply drawn up the desired distance.

If the gases to be collected have a pressure less than the prevailing atmospheric pressure, an aspirator must be used. The simplest form consists of two interchangeable bottles of equal size and the same width of neck. Figure 16 shows an arrangement which may be used when one wishes to take samples at the same time in a gas burette (see p. 35). The water passes from the bottle *A* through the siphon *G* into *C*, and thereby draws the gas from the tube *F*. When *A* is empty, *C*, which is now full, is put in its place, the aspirating of the gas continuing as long as the samples are being taken.

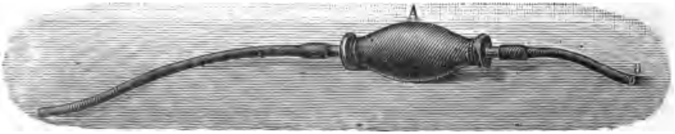

Fig. 17.

Small rubber pumps are also very convenient (Fig. 17). These act both as suction and pressure pumps. The thick-walled bulb *A* is supplied with two simple valves working opposite to each other. When the bulb is compressed with the hand, pressure is produced in one of the tubes, and when the bulb, through the elasticity of the rubber, assumes its original form, suction on the other side results. Either rubber valves or metallic plug-valves are used; the latter have the advantage of retaining their efficiency for many years. It must not be forgotten that gas mixtures are affected by the rubber, and that on this account the apparatus for receiving the gas must be put before the pump.

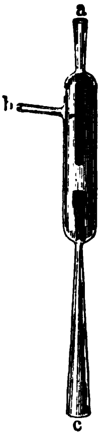

FIG. 18 *a*.

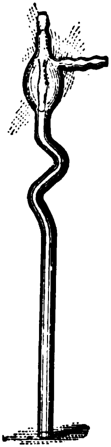

FIG. 18 *b*.

When running water is at hand, a water suction-pump may be used with advantage. The forms proposed by Finkener (Fig. 18 *a*) and by Geissler (Fig. 18 *b*) are among the simplest. In these the water passes under high pressure from the narrow tube *a* into the wider tube *c*, and acts as an injector, thus sucking air in at *b*.

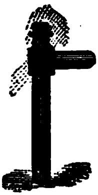

FIG. 19.

A more durable and more efficient form of water-pump is the one constructed by Chapman. This is entirely of brass and has the form shown in Fig. 19.

With such an apparatus as that constructed by Körting,[1] steam also may be used for aspirating.

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[1] Gebr. Körting, Hanover, Germany.

An aspirator of sheet zinc is well suited to the collecting and keeping of large quantities of gas. It consists of a large cylindrical vessel whose conical ends are closed air-tight by stopcocks (Fig. 20).

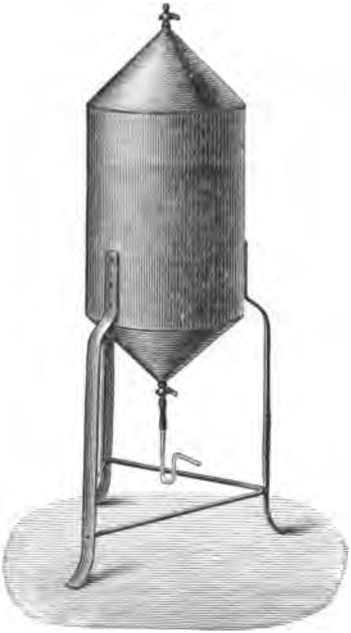

Fig. 20.

If gases are to be taken from a chamber in which excess of pressure prevails, the gas burettes which will be described later may be used directly as aspirators by simply inserting in the rubber tube at the top of the burette a small glass tube, filling this with water, holding it in the current of gas, and then drawing the gas into the burette by lowering the level-tube and opening the pinchcock at the top of the burette.

A gas can be best kept in the fused glass tubes already described, but glass bulbs supplied with two glass stopcocks are also quite satisfactory (Fig. 21).

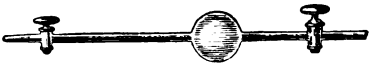

Fig. 21.

Metallic receivers should be used for analytical purposes only when the gas is to remain in them but a short time. They are, however, not easily broken, and are especially well adapted to the transport of large quantities of gas.

Rubber sacks should never be employed, since gas mixtures confined in them rapidly change in composition.

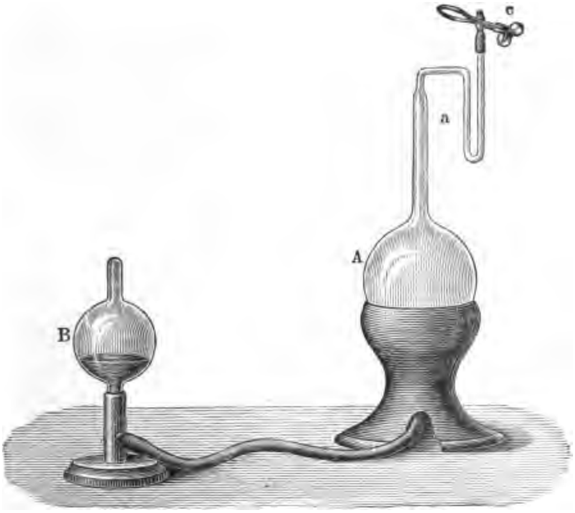

FIG. 22.

If large amounts of gas are to be collected and kept for analysis for a considerable length of time, the portions of gas taken for analysis must be displaced with mercury. It is utterly impracticable to use water for this purpose, for continual changes would take place, since the absorption varies with the pressure and temperature. A gasometer which for years past has given good satisfaction in the Dresden laboratory is shown in Fig. 22. The large glass bulb *A* serves to hold the gas. At the top it carries the bent capillary tube *a*, and at the bottom it is joined to the level-bulb *B* by a rubber tube. The capillary is closed by a rubber tube and pinchcock. The apparatus is first filled with mercury. By lowering or raising the level-bulb, gas can be drawn in or driven out as desired. If gases are to be kept for some time, the capillary tube *a* is filled with mercury by means of a little pipette inserted at *c*. This closes the bulb perfectly. In such an apparatus gases may be kept unchanged for an unlimited time.

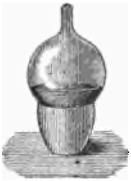

FIG. 23.

Small glass bulbs (Fig. 23) are also very convenient. They are filled with gas in a mercury trough, and are then placed mouth downward in small porcelain crucibles containing mercury. The gas is taken out with the gas pipette to be described later.

A convenient gasometer may be easily constructed from a round-bottomed flask fitted with a two-hole rubber stopper and bent glass tubes in the manner shown in Fig. 24.

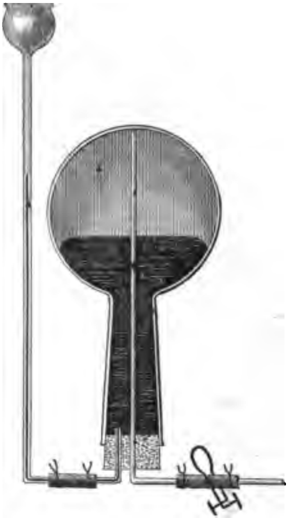

FIG. 24.

Larger volumes of gas may be collected in a glass gasometer of the form shown in Fig. 25.[1] This apparatus is, however, very fragile, and since it is of glass, it cannot be made in large sizes. The reason for the peculiar form of gasometer will be found in the description of Fig. 26.

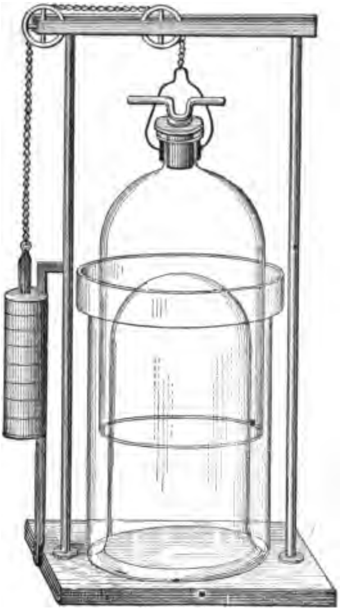

FIG. 25.

For collecting and keeping large samples of gas, a bell gasometer made of zinc or sheet iron and filled with a concentrated solution of magnesium chloride may conveniently be employed. The metal gasometers ordinarily used in laboratories are not practical because the gases stand over large amounts of liquid which must continually be renewed in the filling and emptying of the gasometer, with the result that the gas mixture is contaminated to a considerable degree by the gases which were present in the confining liquid. Figure 26 shows an arrangement which makes it possible to enclose large quantities of gas with the aid of a small amount of a confining liquid. The gasometer consists of the bell *A* which dips into the cylindrical ring-shaped space *B*, this latter being filled with a solution of magnesium chloride. The shaded part

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[1] This may be obtained from Ehrhardt and Metzger of Darmstadt, Germany.

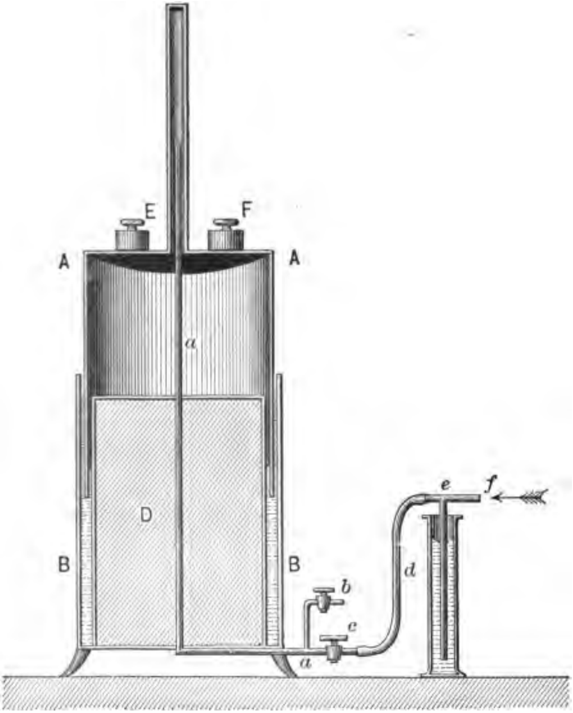

FIG. 26.

D is a hollow cylinder closed at both the top and bottom. The iron tube *a* serves as a guide for the bell and should therefore be made quite wide. The gasometer is filled by introducing the gas in question through *f*. A branch tube at *e* extends downward into a glass cylinder filled with water and serves the double purpose of enabling the operator to observe the pressure of the gas and to drive out any air in the tubes through this branch. The weights *E* and *F* make it possible to regulate at will the pressure in the gasometer. When the gasometer has been filled, the rubber tube *d* is removed from *c*. The gas can then be drawn off through either the stopcock *b* or *c*.

CHAPTER II

GENERAL REMARKS UPON THE ANALYSIS AND MEASUREMENT OF GASES

For the analysis itself various methods, corresponding to the nature of the gases, suggest themselves. The gases may be separated —

1. By successive absorption of the different constituents and the volumetric determination of each.
2. By absorption and subsequent determination by titration or weighing.
3. By combustion and the volumetric or gravimetric determination of the products.

Under all circumstances, however, the first operation is the measuring of the gas.

From the nature of a gas it is clear that its quantity can generally be better determined by measuring its volume than by ascertaining its weight. Hence one of the most important operations in gas analysis is the measurement of gases.

The volume of a gas is influenced by pressure, temperature, and the tension of the liquid present.

By Boyle's law the density and the pressure of a gas are proportional to each other.

According to Gay-Lussac's law gases expand $\frac{1}{273}$ of their volume at 0° for each degree of temperature.

The tension of the confining or absorption liquid causes an increase of volume. This increase is dependent upon the temperature, is independent of the pressure, and varies with the chemical nature of the liquid in question.

To reduce a gas volume, measured in a moist condition, to the volume which it would occupy in a dry state at 0° C. and 760 mm. pressure, the following formula is used: b is the observed barometric pressure, t the temperature, e the maximum tension of aqueous vapour at this temperature, and V the observed volume:—

$$V_o = V\frac{b-e}{760(1+0.00367\,t)}.$$

In very exact work corrections should also be introduced for the expansion of the mercury and glass of the barometer.

Only those volumes can be directly compared with one another that have been reduced to equal pressure and temperature, the tension of the liquid being also allowed for.

Parallel gas measurement can be carried on under—

1. Varying pressure, varying temperature, and varying volume.

2. Constant pressure, constant temperature, and varying volume.

3. Constant temperature, varying pressure, and constant volume.

4. Constant pressure, varying temperature, and varying volume.

In the first case the gas volumes found must be reduced to like temperature and pressure. In the second and third the resulting volumes can be directly compared, since density and pressure are directly proportional.

CHAPTER III

APPARATUS FOR GAS ANALYSIS WITH WATER AS THE CONFINING LIQUID

A. Gas Burettes

1. *The Simple Gas Burette* (Fig. 27)

This consists of two glass tubes, *A* and *B*, which are set in iron feet and are connected by a thin rubber tube about 120 cm. long. To facilitate the cleaning of the burette the rubber tube is divided in the middle and the two ends joined by a piece of glass tubing.

Inside the feet the tubes *A* and *B* are bent at right angles and conically drawn out. The end projecting from the iron is of about 4 mm. external diameter and is somewhat corrugated, so that a rubber tube may be tightly fastened to it by wire ligatures.

The measuring tube *A* ends at the top in a capillary tube *C* of from ½ to 1 mm. internal diameter and about 3 cm. long. Over this a short piece of new black rubber tubing is wired on. The rubber tube is closed, in a completely satisfactory manner, by a Mohr pinchcock which is put on close to the end of the capillary. The author at first closed the burette with a glass stopcock, but experience has shown it to be much easier to make tight connections with rubber tubing and pinchcocks than it is to obtain perfectly tight glass stopcocks. Moreover, the absence of glass stopcocks renders the apparatus less fragile and less costly.

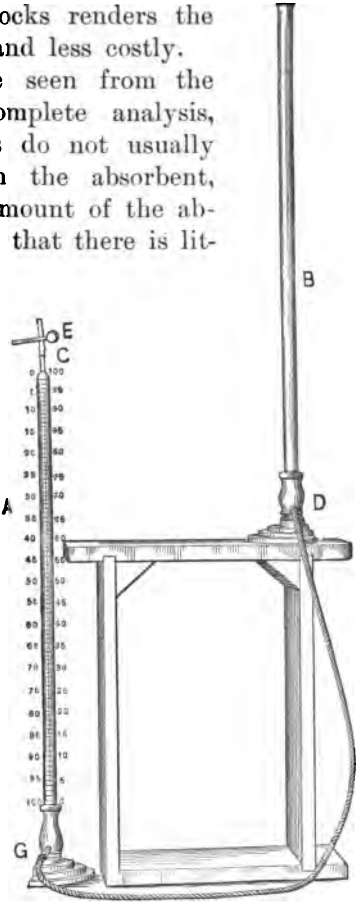

FIG. 27.

Further, as will be seen from the description of the complete analysis, the rubber connections do not usually come in contact with the absorbent, and if they do, the amount of the absorbent is so very small that there is little danger that the rubber will become slippery and slide off from the glass tube. The author would here call especial attention to the fact that, whether glass stopcocks or pieces of rubber tubing are used, they must without fail be tested from time to time to see if they are tight. The pinchcock is always taken off from the rubber tube after using, this helping much to keep the latter in good condition. Notwithstanding the fact that readings cannot be made under the rubber tube, and that the pinchcock cannot always be put on above the tube in exactly the same position, no error results therefrom, since the internal diameter of the glass tube *C* is very small. The author has found that the differences in volume are much less than a tenth of a cubic centimeter, a variation which, in determinations not made over mercury, may be entirely disregarded. The graduated measuring tube *A* contains 100 ccm., the lowest mark being slightly above the iron foot. The cubic centimeters are divided into fifths, and the numbers run both up and down. The tube *B*, which we will call the level-tube, is somewhat widened at the upper end to facilitate the pouring in of liquids.

With the simple gas burette alone an analysis may be made of a gas mixture not too soluble in water, and the author used it with good success before devising the apparatus to be mentioned later. For these reasons the manipulation by means of which it is possible to carry out an analysis with this simplest form of burette will be described.

MANIPULATION OF THE GAS BURETTE

Fill the tubes *A* and *B* with water, taking care to drive all air out of the connecting rubber tube by suitably raising or lowering the tubes; then join the burette to the vessel containing the gas by means of a glass or rubber tube filled with water. (This connecting tube can easily be filled with water by raising the level-tube.)

To fill the burette with the gas to be examined, grasp the tube *B* in the left hand, close the rubber tube at *D* by pressing it between the little finger and the palm of the hand, and pour out the water in *B*.

Place the level-tube on the floor and open the pinchcock *E*. The water will now flow into the level-tube and the gas will be drawn into the burette. When *A* is filled with the gas, close the pinchcock *E*, disconnect *A* from the gas-holder, and after the liquid has run down from the walls of the burette, take up the tubes by the iron feet and by raising or lowering bring the water in the tubes to the same level. The gas is now under atmospheric pressure, and its volume is read off.

To measure off exactly 100 ccm., bring somewhat more than 100 ccm. of the gas into the burette, close the latter with the pinchcock, and let the water run down. Now compress the gas to less than 100 ccm. by raising the level-tube, close the rubber tube at *G* with the thumb and first finger of the left hand, set the level-tube on the table, and raising the burette in the right hand to the level of the eyes, carefully open the rubber tube and let the water run back until the meniscus stands at the 100 ccm. mark. Keeping the rubber tube still compressed, open the pinchcock for a moment; the excess of gas will escape, and there remains in the burette exactly 100 ccm. of gas under atmospheric pressure.

To bring as much as possible of the absorbent into the burette, lower the level-tube until the expanded gas begins to enter the rubber tube, compress the tube at *D* as before described, and pour the water out of *B*. The absorbing liquid is now poured into *B*, and the tube raised as far as the rubber tube permits; in this way a considerable amount of the reagent, diluted with the water in the rubber tube, is brought into the burette.

Compressing the tube at *G*, bring the gas into thorough contact with the absorbent by vigorously shaking the burette. When no further decrease of the volume of the enclosed gas takes place, the reading is made as before described. The difference in volume gives the amount of the absorbed gas.

The advantages of this simple burette over the other similar forms with which the author is acquainted, are the following: —

1. Easier and quicker manipulation, since both tubes may be freely moved, and since the adjusting of the levels does not take place through narrow stopcocks, but on the contrary can be instantly done by raising or lowering the tube.
2. The possibility of bringing the gas under very different pressures by raising or lowering one of the tubes, thus rendering it easy, from the beginning of the analysis, to bring the gas into contact with large amounts of the absorbent.
3. The simple glass tubes can be more easily cleaned, are less liable to be broken, and are cheaper.

In the analysis of gases which are very soluble in water (among these may be classed carbon dioxide except when it is present in very small amounts, as is the case in illuminating gas and some furnace gases), the measurement of the initial volume cannot be made over water, nor over water saturated with the gases. In this case one must use a gas burette which, since it is a modification of the Winkler apparatus, we will call the modified Winkler gas burette.

2. *The Modified Winkler Gas Burette* (Fig. 28)

This consists of the level-tube *a* and the measuring tube *b* connected by a thin rubber tube about 120 cm. long and fastened into iron feet. *b* is a glass tube of about 100 ccm. capacity, provided with the three-way cock *c* and the simple glass stopcock *d*. The space between the two stopcocks is divided into exactly 100 equal parts, and each part into fifths. The thick-walled tube *e* must have an internal diameter of from only ½ to 1 mm., so that bubbles of the gases which are passed in and out cannot stop in the tube.

Instead of the glass stopcock *d* a rubber tube and pinchcock may be used as with the simple burette.

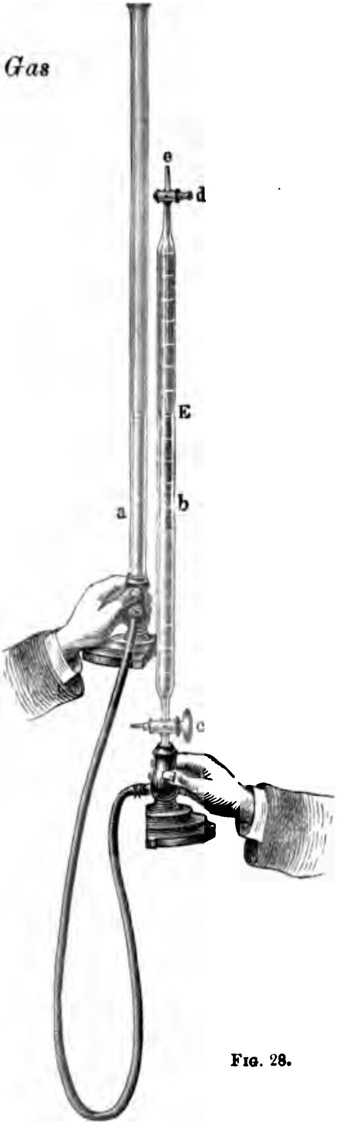

FIG. 28.

Before filling the burette with the easily soluble gases, the tube *b* is first dried by rinsing it out with a few cubic centimeters of absolute alcohol and then with ether, the latter being driven out by aspirating through the tube the gas to be analysed. To do this, join the end *e* of the burette by means of a rubber tube, or better a glass tube, to the vessel containing the gas and bring the three-way cock into such a position that its longitudinal opening communicates with the inside of the burette. Connect the cock with the aspirator. After the gas has been drawn through for a time, close the lower and the upper stopcocks. The gas, if under pressure, is brought to atmospheric pressure by momentarily opening the upper stopcock. The remainder of the apparatus is now filled with water run in through the three-way cock, which is so turned that it communicates with the rubber tube. The water must previously be saturated with those constituents of the gas mixture which are slightly soluble in water. If the mixture contains very soluble gases, *a* and *b* are connected by bringing *c* into the proper position, and the gases are absorbed directly in the burette by shaking them with the water therein. When a mixture contains easily soluble gases, they may be absorbed with water and then determined in the solution by titration. In the analysis of very soluble gases, it is preferable, except in a few rare cases, to lead large quantities of the gas mixture through suitable apparatus containing known amounts of the absorbents, and to determine the quantity of the unused reagent by titration.

The absorbing liquids for determining the constituents which are only slightly soluble in water, are brought into the burette by means of a funnel connected with the longitudinal opening of the stopcock by a piece of rubber tubing.

Beyond this the manipulation is the same as with the simple gas burette.

3. *The Honigmann Gas Burette*

The burette *A* (Fig. 29) contains 100 ccm. divided into $\frac{1}{5}$ ccm., the zero point being at the lower end of the burette. At the top it is closed by a glass stopcock and the lower end below the graduations is drawn out to smaller diameter to permit of a piece of rubber tubing being easily slipped over it. The absorption liquid is placed in a glass cylinder *c*, which should be tall enough to allow the burette to be lowered to any desired point into the liquid. The Honigmann gas burette is suited only to the rapid and approximate determination of carbon dioxide in gas mixtures which contain fairly high percentages of this constituent. In making a determination, the burette is first thoroughly cleaned and dried, and the gas to be analysed is then passed through it until all air in

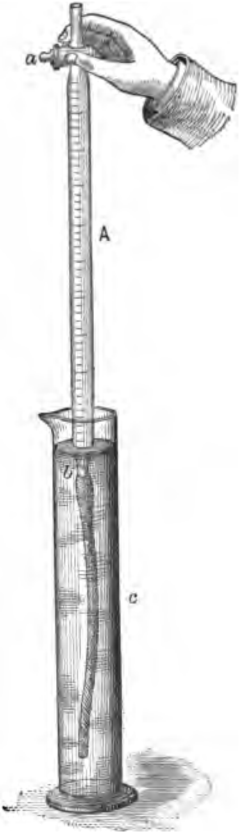

FIG. 29.

the burette has been displaced. Stopcock *a* is now closed and the rubber tube is immersed in a solution of potassium hydroxide in the manner shown in the figure. The solution of potassium hydroxide is made by dissolving one part of commercial potassium hydroxide in two parts of water. The burette is lowered into this solution until the liquid stands exactly at the zero point, and the stopcock *a* is then carefully opened until the liquid inside the burette rises to the same mark. The tube now contains 100 ccm. of the gas at atmospheric pressure. The absorption of the carbon dioxide is effected by grasping the burette between the thumb and fingers in the manner shown in the figure, and turning it downward so that the caustic potash will flow along the walls of the burette and cause the absorption of the carbon dioxide. During this operation the open end of the rubber tube must, of course, remain below the surface of the solution in the cylinder. After all the carbon dioxide has been absorbed the burette is again brought to a perpendicular position and lowered into the liquid in the cylinder until the liquid surfaces on the inside and outside of the burette stand at the same height. The reading is now taken, and the result gives directly the percentage amount of carbon dioxide present in the original gas mixture.

4. *The Bunte Gas Burette*

This consists essentially of the burette *A* and the level-bottle *B* (Fig. 30). The burette is closed at the top by the three-way stopcock *C*, and above this there is the tube *D*, which is provided with a mark about 5 cm. above the stopcock. The lower end of the burette is closed by a simple glass stopcock, and is connected with the level-bottle *B* by a long piece of rubber tubing. A pinchcock is placed upon this rubber tube a short distance below the end of the burette. Inasmuch as all of the readings with this burette will lie between the zero point and the 50 ccm. mark, the instrument is made shorter, and consequently easier to handle, by widening the upper portion. The horizontal opening of the stopcock *C* is closed by a piece of rubber tubing and a pinchcock. The burette and level-bottle are supported on an iron stand of the form shown in the figure, the burette being held in a spring clamp which permits of its easy removal.

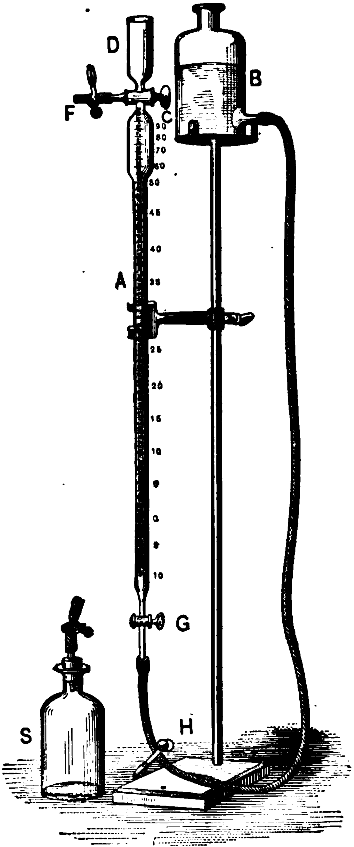

FIG. 30.

The calibration of the burette runs from the zero point, which is near the lower end, up to 100 ccm. at the upper stopcock. The calibration is carried on below the zero point for 10 ccm. There must also be provided a thick walled glass bottle *S* supplied with a one-hole rubber stopper carrying a short piece of glass tubing which is closed by a piece of rubber tubing and a screw pinchcock. A piece of glass tubing bent in the shape ∩ is also necessary for running water into *D*.

Manipulation. — Fill the level-bottle *B* with water, connect the rubber tube with the burette in the manner shown in the figure, open the pinchcock *H* and the two stopcocks of the burette, and allow water to rise in the burette until *D* is partially filled. Close *G* and *H*. Now turn the stopcock *C* until *D* communicates with *F*, and open the pinchcock on *F* until the bore of the stopcock and the rubber tube are filled with water. Then close the pinchcock. Slip the pinchcock *H* up to the lower end of the burette. Close it, and remove the long rubber tube from the burette. Connect *F* with the reservoir containing the gas to be analysed, and open the pinchcock on *F* and the lower glass stopcock of the burette. Place under the burette a beaker to catch the water which runs out. The water in the burette will now flow out, and the gas will be drawn over into the tube. Draw into the burette rather more than 100 ccm. of gas.

The gas in the burette is always read at the pressure of the atmosphere plus the pressure of the column of water standing in *D* up to the mark. For convenience in calculating results it is desirable that the original volume be exactly 100 ccm. at this pressure. To measure off this exact volume close the stopcock *C*, open the pinchcock *H* until the long rubber tube is filled with water, and then slip this carefully over the lower end of the burette, after first making sure that there are no bubbles of gas in the tip of the burette below the stopcock. Now open *H* and *G*, and allow water to rise nearly to the zero point. Close *G*, and then turn *C*, so that *A* communicates with *D*. Since the gas in the burette is under slight pressure, bubbles will escape up through the water in *D*. Bring the water in *D* exactly to the mark, and then by carefully opening *G* allow the water in the burette to rise until it stands exactly at zero. There is now in the burette 100 ccm. of gas under the pressure of the atmosphere plus the column of water in *D*. Close *C*, and proceed to the absorption of the constituent of the gas mixture which is to be determined.

This absorption is brought about by introducing a liquid absorbent into the burette through the lower end. Since these absorbents for the various gases are usually concentrated solutions, it is undesirable to allow the absorbent to be diluted by the water still remaining in the burette between *G* and the zero point. This water is therefore first removed with the aid of the suction bottle *S*. This bottle is connected by means of the rubber tube at its top with a water suction pump, and is exhausted of air. The screw pinchcock is then closed, the long rubber tube is slipped off from the lower end of the burette, and the rubber tube of *S* is slipped over the burette tip. The screw pinchcock on *S* is now opened, *G* is then carefully turned, and the water in the burette is slowly drawn off until it has fallen to a point just above *G*. *G* is then closed, the pinchcock of *S* is closed, and the suction bottle is detached. The reagent to be introduced into the burette is now poured into a small evaporating dish, and this dish is brought up under the tip of the burette; *G* is carefully opened, and the liquid at once rises in the burette. When no more will enter, close *G*, remove the dish, grasp the burette with the thumb and the first two fingers of the right hand at the stopcock *C*, and open the spring clamp with the left hand. Place the first and second fingers of the left hand below the stopcock *G*, pour out the water in *D*, and tip the burette backwards and forwards so that the absorbing liquid will flow along its entire length. Place it again in the clamp, bring the dish of the absorbent under the tip, and allow more liquid to enter if it will, repeating the tilting of the burette in the manner just described. When the absorbent will rise no farther in the burette, that is, when the absorption of the gas is completed, place the burette in the clamp in such a position that its upper end is below the level-bottle *B*, put a beaker under *G*, and insert in the end of the rubber tube of *B* the ∩-shaped glass tube already mentioned. Hook this tube over the edge of *D*. Open the pinchcock *H* so that water will flow into *D*, then open *C*, and lastly open *G*. Water will now flow through the burette and wash out the absorbent, and yet no gas will escape during the operation. When the absorbent has been removed in this manner, close *G*, shut off the supply of water from *B*, and then carefully open *G* until the water in *D* falls just to the mark. Read the volume of gas now remaining in the burette. The difference between this volume and the original volume of 100 ccm. will give the per cent of gas which has been absorbed.

Throughout the entire operation be sure not to touch with the hand any part of the burette except the two stopcocks, since otherwise the heat of the hand would expand the gas in the burette and cause some of it to escape through the open stopcock *C*.

Determinations with the Bunte burette cannot be accurate, since the gas in the burette is brought into contact with large volumes of water which is unsaturated with the gas mixture, and which will therefore absorb some of the gas of the sample. The method is also wasteful of reagent, since the reagent which has once been employed cannot be used over again because of its dilution by the wash water. The use of the burette is limited to the approximate determination of carbon dioxide and oxygen.

B. ABSORPTION PIPETTES

On account of the solubility of gases in water the accuracy of the analysis made by direct absorption in a gas burette is not very great, and the applicability of the method is also limited by the fact that only those absorbents which do not rapidly attack rubber can be used. Further, the apparatus must be cleaned after each analysis, and the absorbing liquid must be frequently renewed.

These disadvantages disappear when the absorption is made in a special apparatus — the gas pipette — as first suggested by Doyère. These gas pipettes contain the reagents, and their construction renders it possible to bring the gases into intimate contact with the absorbents. There must be as many of them as there are absorbable constituents in the gas mixture.

The following forms, varied to suit the nature of the different reagents, are used:—

1. *The Simple Absorption Pipette*

This is a modification of the Ettling gas pipette, first used by Doyère for the absorption of gases, and it is filled with such absorbing liquids as rapidly attack rubber, *e.g.* fuming sulphuric acid, bromine, fuming nitric acid, etc. (see Part II).

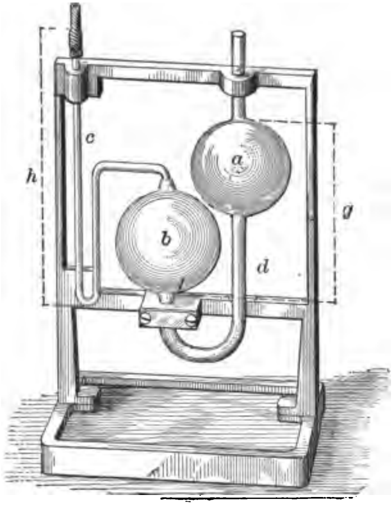

Fig. 31.

It consists of two large bulbs, *a* and *b* (Fig. 31), joined by the tube *d*, and of a capillary glass tube *c*, of ½ to 1 mm. internal diameter, and bent as shown in the figure.

The bulb *a* holds about 100 ccm., and *b* about 150 ccm., so that when 100 ccm. of gas is brought into *b*, sufficient space for the absorbing liquid will remain. To protect the pipette from being broken and to facilitate its manipulation, it is fastened to a wooden or iron standard.

An iron standard of the form shown in the figure is preferable to wood, first, because of its weight, and second, because it cannot warp out of shape; and the iron standard with a four-sided base is better than such a one as is shown in Fig. 37, because with the latter form there is danger that one leg of the pipette may be pushed over the edge of the table and the apparatus fall and be broken.

On account of the different behaviour of wood and glass toward changes of temperature and atmospheric moisture, it is advisable to fasten the glass at only three places by means of metal bands and plaster of Paris, the capillary tube being allowed to project from 2 to 3 cm. above the frame.

A short piece of rubber tubing is wired on to the free end of the capillary. The distance *h* must be greater than *g*, so that it may be possible to enclose a gas between two columns of liquid in the pipette.

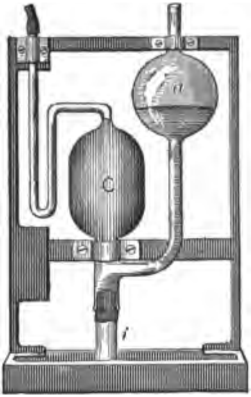

Fig. 32.

2. *The Simple Absorption Pipette for Solid and Liquid Reagents*

The only difference between this and the simple pipette is that in place of the bulb *b* there is inserted the cylindrical part *C* (Fig. 32), which can be filled with solid substances through the neck *i*. A cork or rubber stopper, held in place by a wire, closes the neck *i*.

A glass tube closed at the top, and over which a rubber ring, cut from a rubber tube, is drawn, also makes a good stopper. By this arrangement only a narrow strip of rubber is exposed to the action of the reagent.

DOUBLE ABSORPTION PIPETTES

Reagents which are acted upon by oxygen, *i.e.* alkaline pyrogallol, cuprous chloride, ferrous salts, etc., cannot of course be kept in the above form of pipette, since the reagent in *a* would become inactive in a short time through contact with the air. The author sought to avoid this difficulty by protecting the reagent with a layer of high-boiling petroleum, after first convincing himself that the tension of the petroleum, resulting from its solubility in the reagent, did not cause a perceptible error. It was soon found, however, that although such hydrocarbons lessen decidedly the access of air, they do not by any means form a perfect protection. Further experiment on this subject led to the construction of—

3. *The Double Absorption Pipette* (Fig. 33)

This pipette permits the use of the reagents in question under an easily movable atmosphere which is free from oxygen, and the reagent employed may be kept completely saturated with those constituents of the gas that it does not strongly absorb, this being a great advantage. The pipette consists of the large glass bulb *a*, of about 150 ccm. capacity, and three smaller bulbs, *b*, *c*, and *d*, each containing only 100

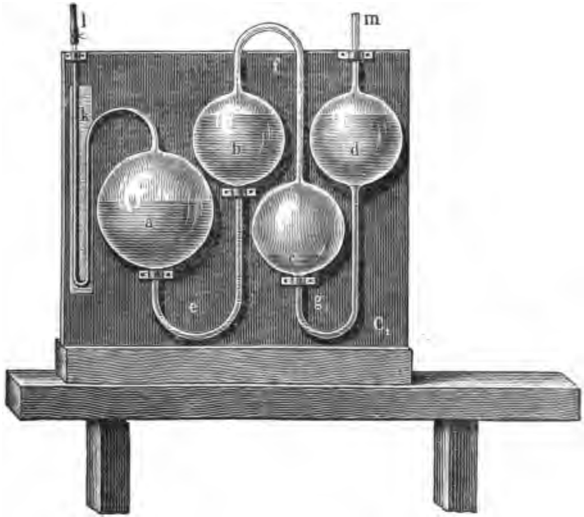

FIG. 33.

ccm. They are connected by the bent tubes, *e*, *f*, and *g*, and end in the bent capillary tube *k*.

The pipette is fastened to a wooden or iron standard in the manner already described (see p. 49).

4. *The Double Absorption Pipette for Solid and Liquid Reagents* (Fig. 34)

The construction may be easily understood from the figure and from what has already been said.

To prepare the double pipettes for use, introduce the solid substance to be employed, and then fill the pipette completely with the gas to be analysed by slowly drawing the gas through. Now pour some water through *m* into the bulb *d* until *g* is full. Close the rubber tube *l* with a pinchcock, insert into it a thin glass tube at least one meter long, and fasten a funnel to the upper end of the latter by means of a piece of rubber tubing.

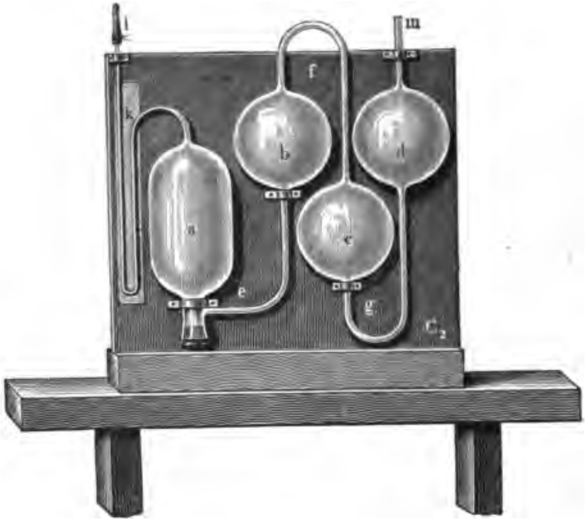

Fig. 34.

Upon pouring the reagent into the funnel, the pressure given to it by the long tube enables it to quickly pass through the capillary tube *k* into the bulb or cylinder *a*. This can be still further hastened by gentle suction at *m*.

After about 100 ccm. of the reagent have been introduced, the bulb *d* is nearly filled with water, and the gas remaining in *a* is driven out through the long tube by blowing into *m*. The pipette is now closed at *l*, and shaken for some time to remove from the bulb *b* the gases absorbable by the reagent. After any gas bubbles which may now be in *a* have been driven out, suction is applied at *m*, and so much gas is sucked out of the bulb *b* that the liquid in *d* will enter and completely fill *c*. If the water first poured in is not sufficient, more must be added from time to time.

In pipettes thus prepared the tubes *k* and *e* and the bulb *a* are filled with the absorbent, the space from *b* to *f* with a gas free from oxygen, *c* and *g* with water, and *d* with air (Fig. 33). While the reagent in the simple pipette may be considered to be saturated with gas only when it is kept in continual use, that in the double pipette, on the contrary, remains saturated for an exceptionally long time, since the diffusion must take place through the confining 100 ccm. of water and through the narrow tube *g*. The error caused by this theoretical possibility may be wholly disregarded in using the pipette.

MANIPULATION OF THE ABSORPTION PIPETTES

To analyse a gas with the apparatus described, the burette is filled with distilled water which has been previously saturated, by shaking, with the gas in question.

If simple pipettes are used, these are so filled with the absorbent that the bulb *a* (Fig. 31) remains empty. The absorbent also must be saturated, by shaking, with the gases which are but slightly soluble in it.

The saturating of liquids is best done in a flask half filled with the same, a rapid stream of gas being led through the liquid, and the flask vigorously shaken.

In technical work, where the same analyses are repeatedly made, the absorbent is kept saturated through continual use.

If the pipettes have the temperature of the room, as can easily be ascertained by introducing a thermometer at *k* (Fig. 35), the analysis is begun by drawing the gas into the measuring tube in the manner already described. It is convenient to take exactly 100 ccm. (see p. 37), so that the results may be read off directly in per cents.

The apparatus is now arranged as shown in the figure.

The pipette is placed on the wooden stand *G*, which has the form shown in the figure. The left-hand end of the base is cut off to permit of the burette being pushed up close to the end of the top of the stand.

The pipette is now connected with the burette by the capillary tube *F*, which is a piece of thermometer tubing of about 0.5 mm. internal diameter. To do this, insert *F* in the rubber tube *m*, slip a piece of rubber tubing about two feet long over the end of *k*, and then, holding *F* in the fingers of the right hand and pressing the rubber tube *d* between the thumb and the first two fingers of the left hand, blow through the rubber tube on *k* until the liquid in the pipette rises to about the middle of the capillary *F*. Then insert the end of the capillary in *d*. If this is properly done, the air enclosed in the capillary should not occupy more than 5 to 10 mm. of its length and the volume may then be disregarded, since the error arising therefrom is about 0.03 ccm. If, however, a greater air volume appears in the

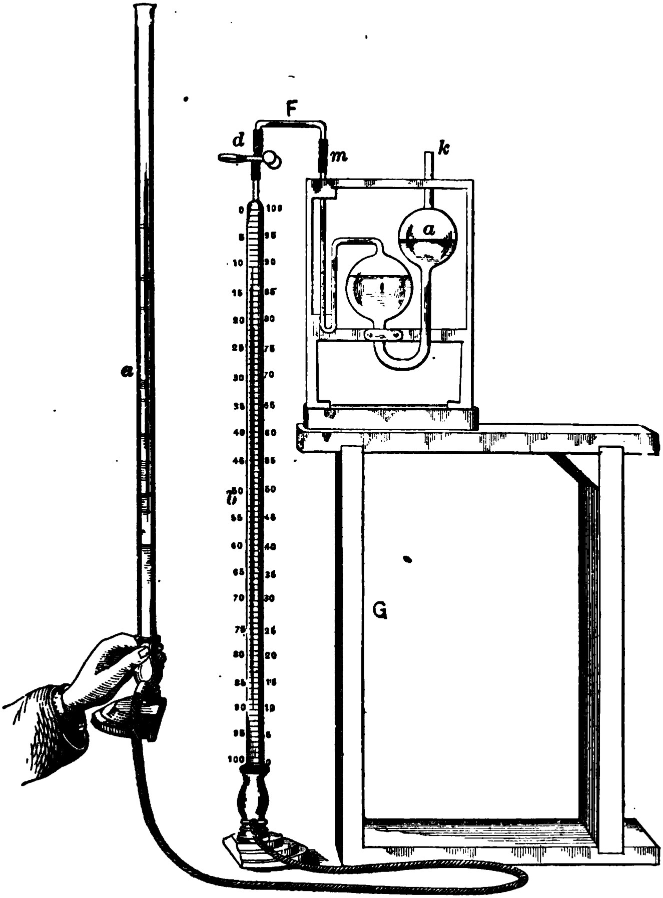
F
d
m
k
a
a
b
G
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

FIG. 85.

capillary tube, *F* should be slipped out of *d* and the operation repeated. In certain cases the reagent should not be allowed to come into contact with the rubber tube at *m*. Under such circumstances the liquid is forced into the capillary of the pipette until it stands just below the top of the iron frame, and the correction for the very small amount of air then introduced can easily be made if necessary. When the pipette and burette have thus been connected, the pinchcock below *d* is opened and the level-tube *a* is slowly raised. The gas is thus driven over into the pipette. Water is allowed to flow through the capillary *F* and the capillary tube of the pipette until it just reaches the top of the first bulb. The pinchcock at *d* is then closed. The gas is now enclosed between two volumes of liquid, the absorbent on one side and the water in the capillary on the other. The gas is allowed to stand in contact with the absorbent until the constituent to be removed has been entirely absorbed. The level-tube is then grasped near the top with the left hand and brought into a lower position than that occupied by the burette *b*. The pinchcock at *d* is then opened and the gas is drawn back into the burette, the liquid in the pipette being allowed to rise to exactly the same point at which it originally stood in *F*. The pinchcock at *d* is then closed, *F* is withdrawn from *d*, and the reading of the remaining gas volume in the burette is made in the manner above described. It frequently happens that complete absorption of the gas can be accomplished only by shaking the pipette after the gas has been driven over into it. In such a case a second pinchcock is placed on the rubber tube *m*, and after the gas has been transferred to the pipette, both *d* and *m* are closed and the right-hand end of the capillary *F* is withdrawn from *m*. The frame of the pipette is now grasped in the two hands, and the absorbent is brought into intimate contact with the gas by shaking the pipette gently backward and forward, *not* up and down. The capillary of the pipette and the tube *F* are still full of water, and when the pipette and burette are again connected and the gas is drawn back into the burette no air is introduced.

The manipulation of the pipettes filled with solid absorbents is still simpler, for in this case no shaking is necessary, because of the large surface of contact between the solid and the gas. On this account also the apparatus need not be disconnected.

A separate pipette is used for each absorbent, and aside from the economy of reagents, the frequent cleaning of the apparatus is thus avoided. An especial advantage is, further, the complete assurance that no loss can take place through ill-fitting glass or rubber stopcocks while the gas is in the pipette or when the pipette is vigorously shaken, and that without fear of error due to the taking up of gases not chemically absorbable, large amounts of reagent may be used, and the work be thereby greatly shortened. After using, the pipettes are closed at *m* with a piece of glass rod, and at *k* with a small cork.

If the absorbing power of the reagent is known (see p. 145), waste may be avoided, and with one filling of the pipette several hundred analyses (the number depending upon the nature of the gases examined) may be made, with certainty throughout as to the efficiency of the absorbent.

If the work has not been carelessly done, the gas burette stands ready for the next analysis. If, on the other hand, reagents have been allowed to enter the burette, it must be cleaned, its simple construction rendering this quite easy.

Some gases are completely absorbed by leading them over into the pipette, while others must remain in the pipette for a certain length of time. By using a small sand-glass, the operator is enabled to give his whole attention to the analysis proper, without fear of allowing too little or too much time to elapse.

CHAPTER IV

APPARATUS FOR EXACT GAS ANALYSIS WITH MERCURY AS THE CONFINING LIQUID

GENERAL REMARKS

ON account of the solubility of gases in water and in the reagents, no great accuracy is attainable, even when these liquids are saturated with the gas mixture being analysed. If very accurate results are desired, the apparatus must unquestionably be filled with mercury. A few years ago it was difficult to obtain glass stopcocks which were perfectly tight, but the manufacture of glass apparatus has been so greatly improved of late that satisfactory instruments can now easily be procured. Complete certainty that the apparatus is absolutely tight can, however, be obtained only by the use of apparatus which contains no stopcocks or rubber connections whatever, and in which all openings are closed by fusing the glass tubes together.

A. APPARATUS WITH RUBBER CONNECTIONS AND GLASS STOPCOCKS

I. Gas Burettes with Correction for Variations in Temperature and Barometric Pressure

Pettersson[1] was the first to show that by means of a tube enclosing a volume of gas it is easy to compensate the error which would result from variations in the pressure and temperature of the atmosphere. Extreme accuracy in gas analysis can be obtained by the use of apparatus filled with mercury, and provided with such a compensating tube, the results with such an instrument being quite as exact as those obtained with the more elaborate apparatus for exact gas analysis described on p. 79, provided always that the stopcocks and rubber connections are perfectly tight. Three different forms of gas apparatus with temperature and pressure correction are shown in Fig. 36, the measuring tubes being varied to accommodate gas volumes of different sizes. Figure 36, I, shows the apparatus intended for the measurement of gas volumes which vary between 0.5 and 100 ccm. Figure 36, II, may conveniently be used when the gas volume amounts to about 150 ccm. In Fig. 36, III, is shown an instrument which was specially constructed for the examination of gases evolved from bacteria, the gas volumes usually amounting to about 10 ccm.

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[1] *Zeitschrift für analytische Chemie*, **25**, 467–484.

The instruments consist of the graduated measuring tubes *A*, the correction tubes *B*, the manometer tubes *F*, and the level-bulbs *G*. The measuring tubes and level-bulbs are mounted in suitable iron feet. The measuring tubes and the correction tubes stand in the wide glass cylinders *C*, which are filled with water to insure that these two tubes are at all times at the same temperature. The measuring tubes are closed at the top by a double Greiner-Friedrich glass stopcock, the construction of which is shown in Fig. 36, IV.

The correction tube *B* and the manometer tube *F* are made from simple glass tubes fused together in the form shown in the cut. g is a small capillary tube. The manometer tubes are U-shaped, and are somewhat widened at k and i, these two widened portions having marks scratched on the glass at exactly the same height. The manometer tube is joined to the measuring tube by means of a piece of rubber tubing connecting the end of the capillary l with the tube a of the stopcock. The reason for making the manometer tube so long lies in the fact that otherwise, if the apparatus is carelessly handled,

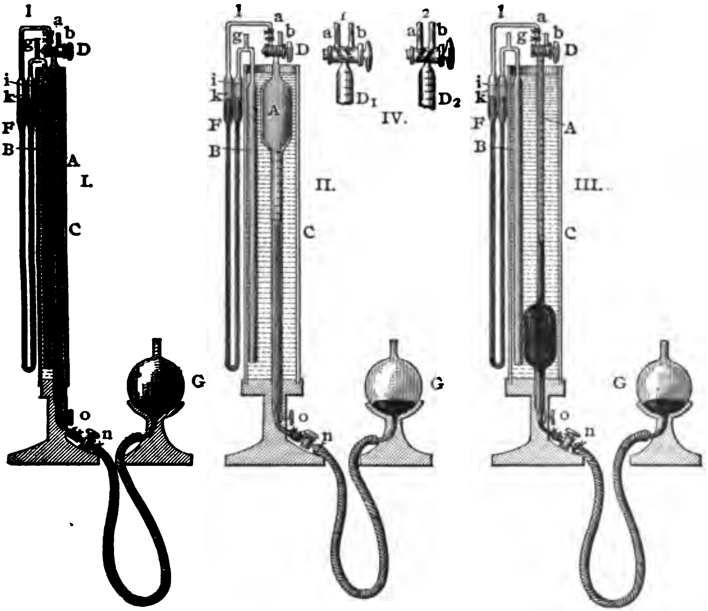

FIG. 36, I-IV.

the mercury might easily be driven from the manometer tube into the burette or the correction tube. With the arrangement shown in the figure this is almost impossible, since the difference in pressure must be more than half an atmosphere before the mercury can pass over into either tube. The manometer tube is made completely from glass to prevent the mercury being contaminated with the dirt from the interior of a rubber connection. If the burette has become dirty, the manometer tube is removed, and the rest of the instrument may then be cleaned without danger of any change taking place in the gas volume enclosed in the correction tube.

To prepare the apparatus for use, draw some distilled water through the capillary *g* into the correction tube *B*, and also moisten the walls of the measuring tube *A* with a drop or two of water. Fill the level-bulb *G* with mercury, and turn the glass stopcock to the position shown in D_1. Then by raising the level-bulb drive the mercury over into the manometer tube until the latter is filled up to the marks on *k* and *i*.

Before proceeding with the analysis, the volume of the manometer tube from the mark on *k* to the point *a* must be ascertained. To do this, draw over the mercury in the manometer until it reaches *a*, then turn the stopcock *D* until it has the position of D_2, and now draw any desired volume of air into the burette. Leaving the stopcock open, read off this volume of air on the scale of the burette, the air here being, of course, under the prevailing pressure of the atmosphere. Turn stopcock *D* so that the burette communicates with the manometer tube, and drive the air over into this latter tube until the mercury in it stands at equal height in its two branches; that is, at the marks on *k* and *i*. The difference between the two readings on the measuring tube, provided the tube *g* remains open, gives the volume of the manometer from the mark on *k* up to *a*.

Correction tube *B* may be used in either of two ways. We may enclose within it an indeterminate amount of air by simply fusing together the end of the tube *g* so that the volume in the correction tube will correspond to the barometric temperature and pressure prevailing at the time of operation, or we may fill *B* with such an amount of air that the apparatus will indicate directly gas volumes reduced to standard conditions,—that is, to 0° C. and 760 mm. pressure. In the latter case, the gas will have at the ordinary temperature of the room a pressure somewhat above that of the atmosphere. In the former case the barometer and the thermometer must be read at the time the tube *g* is fused together, so that we may be able to correct gas volumes whenever this is necessary.

In many cases it is highly desirable to so arrange the apparatus that the reading on the measuring tube *A* corresponds directly to volumes at 0° C. and 760 mm. pressure. To accomplish this a piece of rubber tubing is slipped over the end of the capillary tube *g* and fastened firmly in place by a wire ligature. By lowering the level-bulb, mercury is drawn over into the manometer tube until it reaches the capillary *l*, and the burette is then allowed to stand for two hours in a room of fairly constant temperature. The stopcock *D* is then opened so that the contents of the burette are in free communication with the atmospheric air. As soon as one is convinced that all parts of the apparatus are at the same temperature, the gas volume in the burette is read exactly, and the temperature and barometric pressure are noted. The thermometer and barometer should stand in the same room with the apparatus. The stopcock *D* is closed and the volume which the gas would occupy at 0° C. and 760 mm. barometric pressure is now calculated.

Example. — The gas volume is 97 ccm., the barometric pressure 753.3 mm., and the temperature 8.75° C. The space from *k* to *a* in the manometer has previously been determined and found to be 1.8 ccm. The tension of the water vapour at 8.75° C. is 8.4 mm.

If b represents the observed barometric pressure, t the temperature, e the tension of water vapour at that temperature, and V the observed volume, the volume V_0 which the gas would occupy under standard conditions may be calculated from the following formula: —

$$V_0 = V \frac{b - e}{760\,(1 + 0.00367\,t)}.$$

In the above example this volume is 92.1 ccm.

Since, however, in making measurements with the correction tube the gas fills the space from *k* to *a*, this volume must be subtracted from the above result: —

$$92.1 - 1.8 = 90.3 \text{ ccm.}$$

In order now to adjust the gas volume in the correction tube so that readings of volumes in the burette will be reduced at once to standard conditions, the stopcock *D* is turned so that the burette communicates with the manometer tube, and the gas volume in the burette is compressed by raising the level-bulb *G* to the volume which it has been calculated that it would occupy at 0° C. and 760 mm. pressure. The mercury in the manometer tube is, of course, forced out of equilibrium by this operation. Air is now blown into the correction tube through the rubber tube at *g* until the mercury stands at the same height in the two branches of the manometer tube, and the rubber tube is then closed by means of a strong pinchcock placed directly above the end of *g*.

A rubber tube cannot remain tight for any length of time, and therefore the glass tube *g* must be fused together. This cannot be done at once because of the high pressure of the air in the correction tube, but the operation can easily be performed by first removing the rubber tube joining the manometer tube with the burette at *a* and then placing the correction tube *B* in a freezing mixture of salt and ice, allowing it to stand therein until the mercury in the manometer shows that the pressure on the inside of the correction tube is smaller than that of the external atmosphere. The tube *g* can now be heated by means of a blast lamp and drawn out and fused together directly below the rubber tube which is upon it.

There is danger that the glass tube *g* may crack when it is heated. This can be avoided by painting it with a thin emulsion of plaster of Paris stirred up with water, leaving the place where the tube is to be drawn out uncovered by this coating. The plaster of Paris offers an excellent protection against the overheating of that part of the glass tube which it is not desired to soften and can afterward easily be removed with the aid of water.

The correction tube, after being thus adjusted, is again joined to the burette. The readings of gas volumes in the burette now give directly the volumes under standard conditions, no matter how great may be the variations of temperature and pressure, provided always that in making the measurements the stopcock is turned to the position of D_1 and the mercury in the manometer tube is brought to the marks *k* and *i* by expanding or compressing the gas in the measuring tube. The exact adjustment of the mercury in the manometer tube is effected by raising or lowering the level-bulb *G* until the mercury stands nearly at the marks *k* and *i*, then closing the stopcock *n* and turning the screw *o* so as to exert greater or less pressure on the piece of rubber tubing against which it plays. This piece of rubber tubing, as is shown in the figure, connects the lower end of the burette with the stopcock *n*. In this manner the surface of the mercury in the two arms of the manometer may be brought exactly to the same level. This style of adjustment is original with Pettersson and enables us to effect slight changes in the size of the gas volume in a most convenient and rapid manner. In all cases where rubber tubing must withstand considerable pressure it is desirable to use the so-called "patent" rubber tubing which, although not quite as elastic as the ordinary kind, will easily withstand a pressure of several atmospheres.

II. The Absorption Pipettes

On account of the great differences in pressure caused by columns of mercury of only moderate height it becomes necessary to give to these absorption pipettes, which are partially filled with mercury, a form somewhat different from that adopted for the pipettes containing aqueous solutions.

1. *The Simple Mercury Absorption Pipette*

This consists of two bulbs, *a* and *b*, Fig. 37, joined together by a piece of patent rubber tubing. The bulb *a* has a capacity of about 110 ccm., and *b* a capacity of from 120 to 150 ccm.

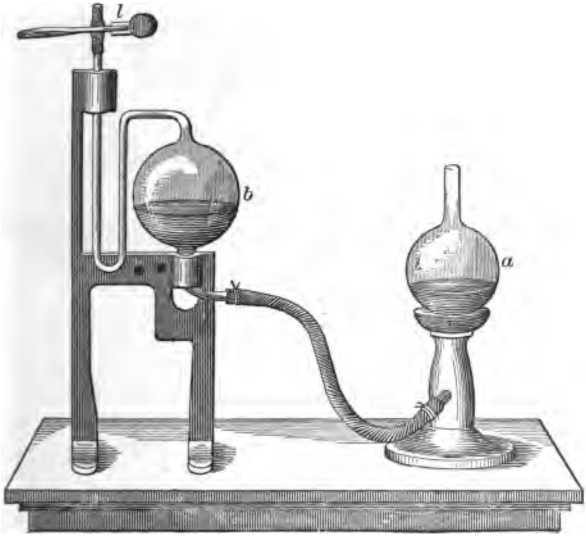

FIG. 37.

2. *The Simple Mercury Absorption Pipette for Solid and Liquid Reagents*

This resembles the pipette just described, except that the bulb *b*, Fig. 38, is cylindrical in form and has at its lower extremity a cylindrical neck, *i*, through which the bulb can be filled with solid substances. *i* is then closed with a cork or rubber stopper held in place by a wire ligature.

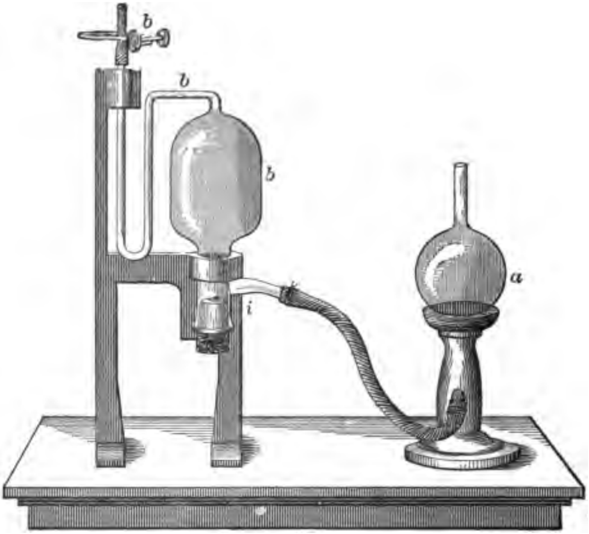

FIG. 38.

3. *The Mercury Absorption Pipette with Absorption Bulb*

This pipette has in addition to the two bulbs *a* and *b*, Fig. 39, a third bulb *c* filled with broken glass or with glass beads. The advantage of this small bulb lies in the fact that when the gas is driven over into the pipette, the reagent which the latter contains clings to the small pieces of glass in *c*, and causes a more complete absorption of that constituent of the gas mixture which is to be removed. The pipette has, however, one drawback: with viscous reagents bubbles of gas are liable to cling to the broken glass in *c*.

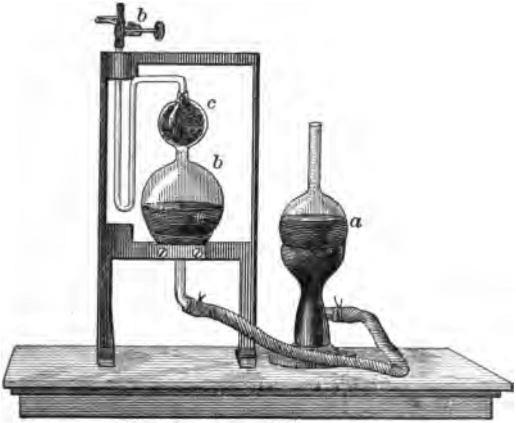

FIG. 39.

The mercury pipettes are manipulated in exactly the same manner as the pipettes for aqueous solutions above described, except that here only small quantities of the reagent are employed, in order to reduce to a minimum the error which is caused by the solubility in the reagent of those gases which are not directly absorbed by it. This error can be completely avoided by introducing into the gas pipette an amount of reagent sufficient for two analyses of the gas mixture in question. In the first analysis the reagent becomes saturated with those gases for which it is not an absorbent, and the error due to solution of the gases in the reagent is thus completely avoided in the second analysis. The reagents are introduced into the gas pipette by means of a small pipette inserted in the rubber tube *b*.

If it is desired to avoid completely the error caused by the introduction of the small quantity of air when the connecting capillary of the form shown in Fig. 35 is used, the gas pipette and gas burette may be joined by means of a three-way capillary in the manner shown in Fig. 40. With the aid of the small separatory funnel, it is possible to remove the last trace of air from the capillary by simply driving the reagent as far as the bore of the stopcock before opening the stopcock of the burette.

One of the chief advantages of the apparatus described in the foregoing pages consists in the exact compensation of any variations in the temperature of the room. In the opinion of the author the gas volumeter of Lunge is faulty in construction because of the three tubes of which it is composed. The measuring tube and the compensation tube are not immersed in one and the same column of water, and since air is a poor conductor of heat, two tubes standing free in the air assume the same temperature, only very slowly. The errors which result from variations in temperature are precisely the ones most to be feared. The temperature of an apparatus may easily be raised 1° C. by the heat from the body of the experimenter, and frequently this rise in temperature is considerably more than 1° C. A gas expands $\frac{1}{273}$ of its volume when its temperature rises 1°, the error thus caused being about 0.3 per cent, while a change in pressure of 1 mm. causes an error of only $\frac{1}{760}$ of the volume; that is, 0.13 per cent. The author is therefore of the opinion that all forms of measuring apparatus which are to be used for rapid, and at the same time exact work, should unquestionably be provided with water jackets.

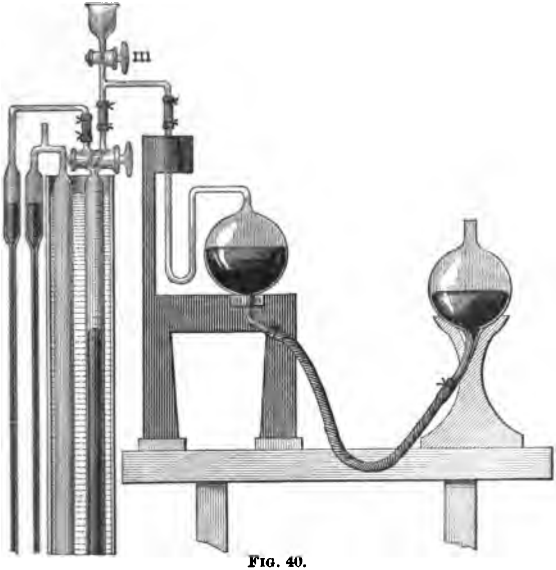

FIG. 40.

III. Gas Evolution Apparatus

The apparatus devised by Scheibler and the azotometer original with Knoop were among the first instruments which permitted of the easy measurement of volumes of gas set free from a weighed amount of the substance. The Scheibler apparatus has been materially improved by Finkener, and the azotometer by Wolf, Dietrich, G. Wagner, and F. Soxhlet. The gas volumeter, original with Lunge, makes automatic correction for variations in pressure, and has been recommended for the evaluation of pyrolusite and chloride of lime, and the determination of hydrogen peroxide and potassium permanganate.

With all of these forms of apparatus, the procedure consists in setting free a gaseous constituent from a weighed amount of the substance, and then exactly measuring the volume of the evolved gas.

A most convenient and accurate azotometer is obtained by using a burette with temperature and barometer correction in conjunction with a gas evolution apparatus, as is shown in Fig. 41. A special advantage of this apparatus lies in the fact that it permits of the direct reading of the evolved gas under standard conditions; that is, the gas in the burette is automatically reduced to the volume which it would occupy at 0° and 760 mm. pressure. In Fig. 41 is shown the burette, already illustrated in Fig. 36, II, but, of course, the burette shown in Fig. 36, I, can just as well be used. The gas evolution apparatus corresponds to that employed in the usual form of azotometer, and consists of the glass bottle *q* provided with a perforated glass stopper. A wide glass tube, filled with pieces of broken glass, or with glass beads, is inserted in the opening of the stopper, and the upper end of this tube is connected with the capillary *b* of the stopcock *D* by means of a piece of rubber tubing of small bore. To permit of simultaneous communication between the bottle *q*, the burette *A* and the correction tube *B*, the stopcock is removed from the collar, and both ends of the opening are closed with short rubber stoppers, which are held in place by a wire ligature passed around them.

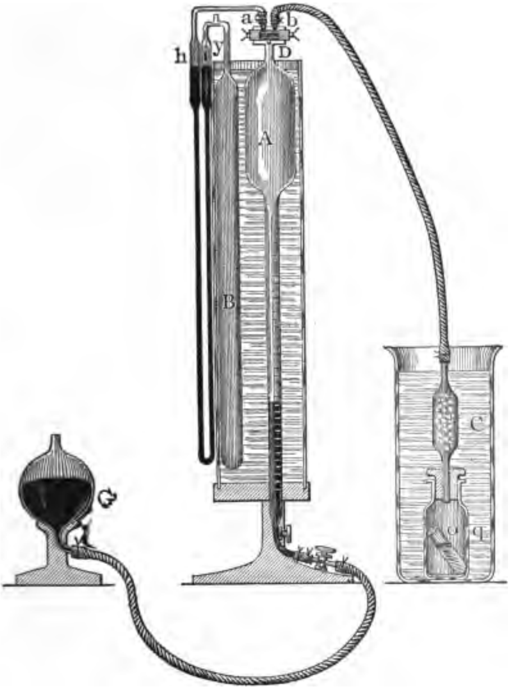

FIG. 41.

To determine with the aid of the apparatus thus arranged the amount of a gas which is set free when a liquid is brought in contact with a solid substance, a weighed amount of the substance is placed in the bottle *q*, the liquid which is to act upon the substance is placed in the tube *o*, and this tube is then carefully lowered into the bottle. The stopper of the bottle is now inserted and is held in place by means of a wire ligature. The bottle is lowered carefully into a large beaker *C* filled with water of the temperature of the room, and the initial volume of the gas in the burette is read off, the mercury in the two arms of the manometer tube being of course first brought to the same level. The bottle *q* is now tipped so that liquid flows from *o* upon the substance, and the bottle is shaken until no further change of gas volume can be noticed on the scale of the burette. The difference between the initial and the final reading on the burette gives the corrected volume of the evolved gas.

In the determination of gases which are set free only when the liquid is brought to boiling, an apparatus of the form shown in Fig. 42 may be employed. Figure 42, IV, is the gas evolution apparatus; Fig. 42, II, a burette with temperature and barometer correction. The gas evolution apparatus consists of a flask *R* and the condenser *S*. The flask has a side tube *T* which is closed by means of the tube *m* provided with the stopcock *n*. The lower ends of both the condenser *S* and the tube *m* are carefully ground into the tubes in which they fit. In using this apparatus the substance is placed in the flask *R*, this flask is then exhausted of air through *k* by means of a water suction pump, and the reagent is brought into *R* by pouring it into *T* and carefully lifting the tube *m*. The gas in question is then set free by boiling, and is completely driven over into the burette by running in liquid from *T*. If several gases are simultaneously evolved, they may be passed into different absorption pipettes and the amount of each determined.

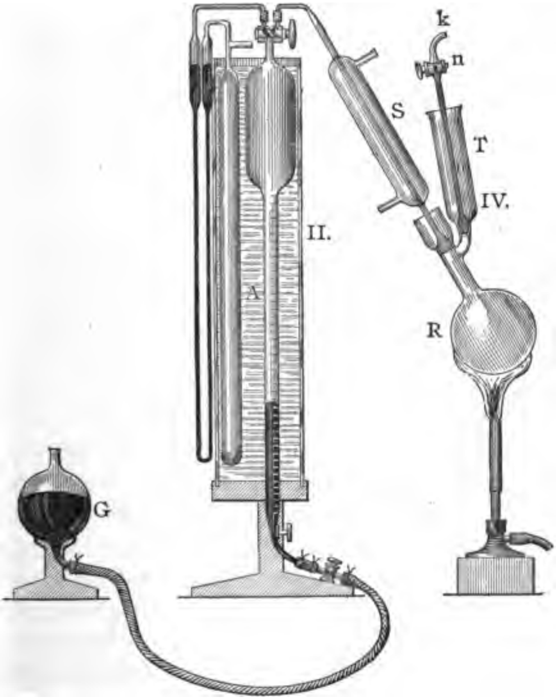

FIG. 42.

(See the determination of fluorine in the presence of carbon dioxide, p. 378; and of carbon in iron, p. 459.)

B. Apparatus for Exact Gas Analysis without Rubber Connections or Stopcocks

Experience has shown that even the best glass stopcocks cannot be relied upon with certainty for any considerable length of time, and rubber connections will gradually allow small quantities of gas to pass through them. It is therefore apparent that an apparatus which contains no stopcocks or rubber connections whatever possesses decided advantages over one in which errors arising through leakage are liable to occur.

The wonderfully simple and exact gasometric methods devised by Bunsen fulfil completely these demands, but unfortunately the rapid performance of a large number of exact analyses is not possible with his apparatus.

The method devised by Doyère[1] resembles that of Bunsen, in that the analysis is carried out in glass vessels fused together, and all ground joints and rubber connections are avoided: it has, however, the fault that great accuracy can be obtained only by the use of very cumbersome apparatus.

By the introduction of a different manner of measuring and a somewhat changed construction of the necessary absorption pipettes, the author has endeavoured to improve the Doyère method, so that, in its changed form, rapid and very exact work may be possible without the use of delicate physical instruments.

Bunsen measures the gases under varying pressure and varying volume, and Doyère measures them under constant pressure and varying volume, while in the method about to be described the measurements are made under constant volume and varying pressure. Following Mariotte's law, the values so found bear the same proportion to one another as do gas volumes under the same pressure.

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[1] *Ann. Chim. Phys.* [3], **28**, p. 1.

If the gases are saturated with moisture when measured, corrections for the tension of aqueous vapour are unnecessary.

Doyère[1] measures the gases in a Bunsen eudiometer, and he avoids correction for pressure by joining the eudiometer with an iron holder having a screw attachment, by means of which the mercury in the tube and in the suitably formed trough may be brought to the same level. The readings are made with a special telescope of great exactness. The absorptions are effected in Doyère's improved Ettling gas pipette.

The manipulation of the pipettes demands that the eudiometer at some place in the mercury trough be brought wholly beneath the level of the mercury, and further, that the suction tubes of the pipettes be as long as the eudiometer. From these two particulars it results that when a very deep trough is used, the pipettes are very unwieldy and easily broken, or that when a shorter eudiometer is employed, a sharp reading of the scale can be made only with the most perfect instruments, since it must be possible to measure with exactness tenths of a millimeter.

Doyère states that the measuring tubes used by him have a length of 20 cm. and an internal diameter of 15 mm. For large gas volumes he uses vessels similar to those employed by Bunsen for this purpose, the lower part being cylindrical and graduated, and ending above in a bulb.

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[1] *Ann. Chim. Phys.* [3], **28**, p. 1. Fehling's *Handwörterbuch der Chemie*, vol. 1, p. 512.

The method here to be described permits, by the employment of spherical measuring vessels, the use of a shallow mercury trough and of shorter, more easily manipulated, and less fragile gas pipettes, and a measurement more than three times as sharp, since with this apparatus, if the gas at the beginning of the analysis nearly fills the bulb at atmospheric pressure, the scale has an available length of 760 mm. while Doyère's measuring tube is only 200 mm. long.

The measurements are made at constant volume, varying temperature, and varying pressure. This is accomplished by placing the gas in small glass bulbs which can easily be brought into communication with the manometer tube, by then expanding the gas to a certain volume by lowering a movable vessel filled with mercury, and finally reading on the manometer tube the pressure under which the gas now stands. According to Mariotte's law the values thus obtained bear the same proportion to one another as do gas volumes under the same pressure.

The corrections which are made necessary by the changes in temperature and in the pressure of the atmosphere are ascertained in a simple manner by the use of a correction tube.

The absorptions are effected in gas pipettes to be described later.

In the two preceding editions of this book there was described an apparatus which was provided with a barometer tube and with which analyses could be made without the introduction of any correction whatever, provided the whole apparatus were kept at constant temperature by means of running water. The author is now convinced, however, that with the use of a correction tube just as accurate results can be obtained as with the more complicated apparatus, and he regards it as in general undesirable to construct large pieces of apparatus which have many connections, since in time all rubber becomes bad, the iron parts of the apparatus rust, and the mercury becomes contaminated. The apparatus should be so designed as to permit of the easy removal and replacement of any of its parts. The author therefore regards such pieces of apparatus as the different forms of the Orsat as unpractical, since here a large number of absorption vessels are joined together by means of several complicated connections.

DESCRIPTION OF THE APPARATUS BY W. HEMPEL

The apparatus (Fig. 43) consists of an iron mercury trough *A* (on account of the presence of water, wood cannot be used, since it would swell and change form), of a glass tube *D* graduated in millimeters and from 76 to 80 cm. long, and further, of the wooden stand *G* and the water reservoir *E*. The sides of the water reservoir *E* are glass panes, one of which *e* extends only so deep into the mercury as to leave room to bring the capillary of the pipette *B* under it into the measuring bulb *C*.

By placing the measuring bulb upon the rubber stopper *a* in the mercury trough it can always be brought, by means of the holder *f*, into mercury-

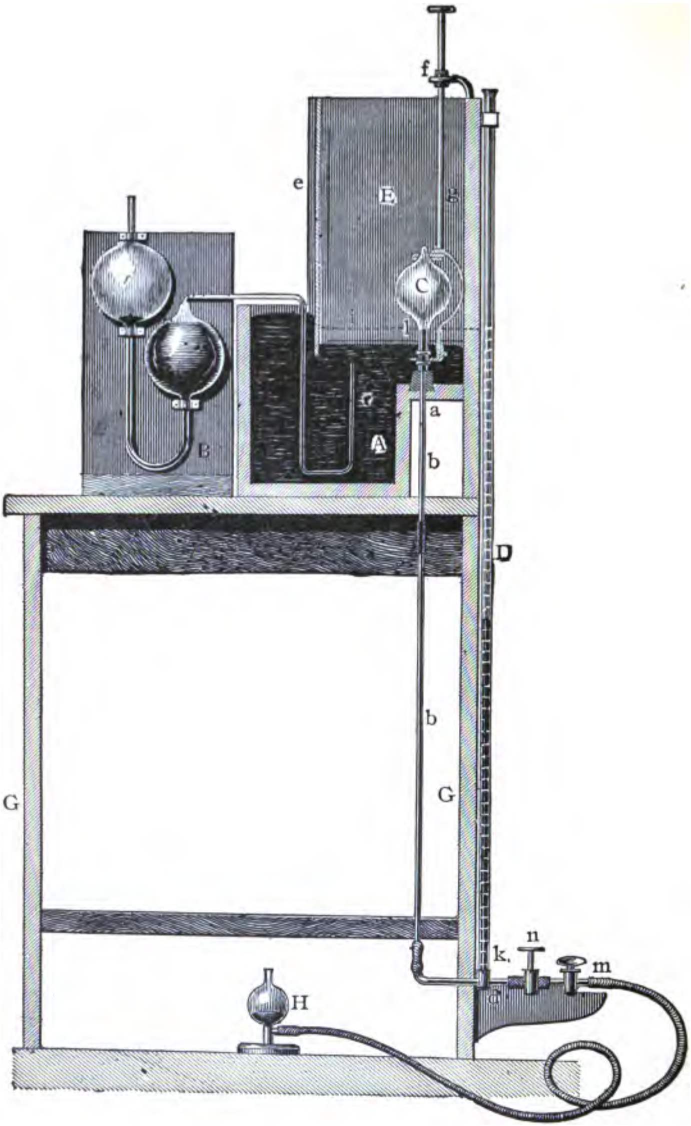
f
e
E
g
C
a
A
B
b
b
D
G
G
k.
n
m
d
H

Fig. 48.

tight connection with the graduated tube *D*. The tube *b* and the ⊥-piece *d* are made of iron. *D* is connected with an arm of *d* by means of a piece of strong patent rubber tubing, or ordinary rubber tubing so wrapped as to enable it to resist the pressure of the mercury. A piece of patent rubber tubing joins the other arm to the movable level-bulb *H*, but between *d* and *m* there is introduced the Pettersson device for the fine adjustment of the mercury. (See Fig. 36.)

In making the measurement, the measuring bulb *C* is brought into the position shown in Fig. 43, and is pressed down tightly upon the rubber stopper *a* by means of the clamp *f*. Mercury is then drawn out through *d* until the meniscus of the mercury in the measuring bulb lies nearly tangent to the horizontal hair of a magnifying glass which is fastened to the apparatus opposite *l*. This glass is not shown in the figure. *m* is then closed and the exact adjustment of the height of the mercury at *l* is effected by turning the screw *n*.

The height of the mercury in the manometer tube *D* is now read with a cathetometer, and the pressure of the gas in the bulb is thus determined. After first introducing corrections for variations in the temperature, the pressure of the surrounding atmosphere is ascertained by means of the correction tube described on p. 94 and shown in Fig. 53.

THE MEASURING BULB

The measuring bulb *E* (Fig. 44) is fastened to the iron holder *g* by means of the projecting tubes *r* and

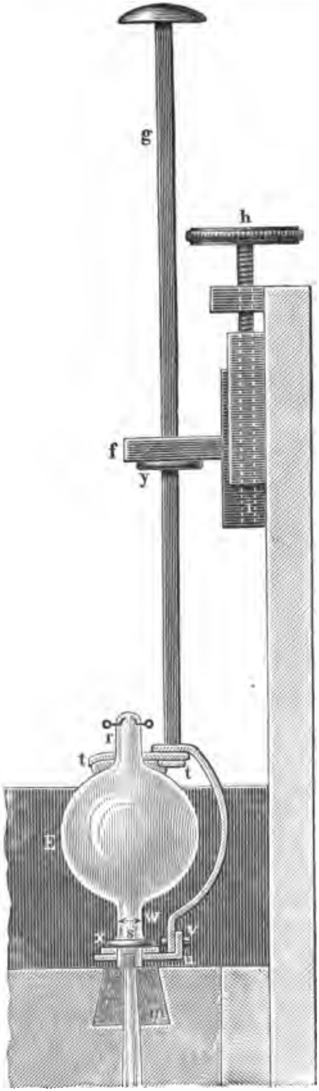

Fig. 44.

s; *r*, which is closed at the top, is about 5 mm. long and *s* about 30 mm. At from 5 to 7 mm. below the bulb, *s* is widened into a collar *x* by softening the glass tube in the blast-lamp flame and pressing it together. The iron holder *g* has at *t* a thick perforated sheet-iron cap for holding *r*. The holder bends around the bulb and is supplied at the lower end with the perforated iron plate *u*, which is bent at a right angle, and holds the projection *s*. *u* may be set where desired by means of the screw *v*, to which the slot through which it passes gives a play of several millimeters. *s* projects 4 to 5 mm. beyond the plate *u*. The iron collar *y* is fastened to *g* in such a position that it just slips under the fork *f* when the holder and bulb are placed over the end of the iron tube passing through the rubber stopper *m*, and are firmly pressed against the rubber. The fork is firmly fastened to the slide *i*, which can be moved up and down by the screw *h*. By screwing the slide down, the measuring bulb can be pressed against the rubber stopper and a tight connection with the barometer tube thus be obtained. A scale upon the slide *i* and its guides makes it possible to bring the bulb at different times into exactly the same position as regards the millimeter scale of the barometer.

The total height of the measuring bulbs varies from 7.5 to 9.5 cm.

Since the walls of the measuring bulbs used by the author are only as thick as those of ordinary bulb pipettes, it was thought possible that, in the measurement of very small gas volumes, the volume of the bulb might be decidedly changed, since under such conditions it is exposed to nearly the full pressure of the atmosphere.

To settle this question, the volume of the bulb, first empty and then filled with gas, was determined in a stereometer, and it was found that even with large bulbs of 100 ccm. capacity no measurable difference of volume could be detected; hence even thin-walled glass bulbs may be used without hesitation for these measurements.

Curiously enough, it is quite difficult to lower the measuring bulb through the water in *E* (Fig. 43) down into the mercury below without some water getting into the inside of the bulb. If this should happen, exact reading would, of course, be impossible. The operation can be performed, however, by bringing the measuring bulb into two porcelain crucibles placed one within the other in the manner shown in Fig. 45, and then filling these two crucibles with mercury. When these are lowered through the water into the mercury the larger crucible *A* is first removed, and then the crucible *B* is lowered away from the mouth of the bulb. The opening in the bulb is now below the surface of the mercury, and yet no water has entered it.

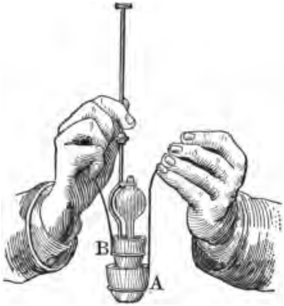

Fig. 45.

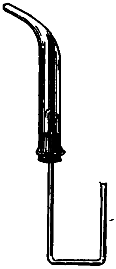

Fig. 46.

By means of the instrument shown in Fig. 46 the air may be sucked out of the measuring bulb, and the gas sample can then be transferred to the bulb by means of one of the pipettes described below.

The Gas Pipettes

The gas pipettes were devised by Ettling and were first used by Doyère as absorption vessels for gas analysis.

They consist of two bulbs *a* and *b* (Fig. 47), of the same size, joined together by the tube *c* and ending in the bent capillary tube *d*. A very small bore thermometer tube, and not a tube of 1 mm. bore as Doyère suggests, is used as the capillary, thus making it easy to avoid introducing absorbent into the measuring bulb or leaving of any considerable quantity of gas in the pipette.

Gases move rapidly in capillary tubes, but liquids, especially concentrated solutions of salts, move very slowly; hence it is easily possible to bring the gas residue in the pipette to less than $\frac{1}{1000}$ of a cubic centimeter without danger of the absorbent entering the measuring bulb. It is almost impossible to do this when wider glass tubes are used.

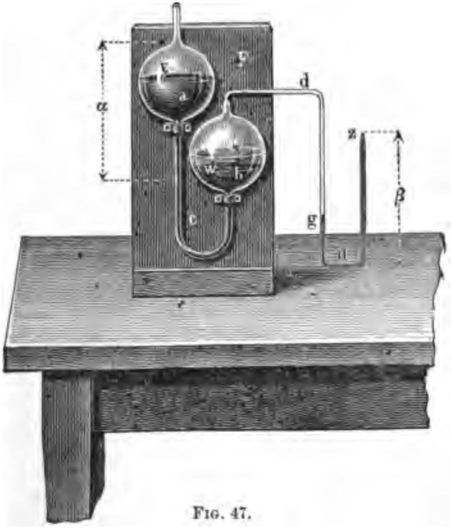

FIG. 47.

The pipettes must be so made that the distance *a* (Fig. 47) is only as large as or smaller than *β*: the capillary must be bent close to the bulb *b*. The pipettes are fastened to the wooden standard in such a position that the capillary *d* comes to within a few millimeters of the bottom of the mercury trough when the pipette is placed in the position shown in Fig. 43.

The bulbs of the pipettes must be considerably larger than the volume of the gas to be brought into them. The inconvenience of carefully cleaning the pipette after the absorption is avoided by using a special pipette for each reagent. Pipettes of very different sizes are employed, the sizes depending naturally upon the dimensions of the measuring bulbs.

To bring a measured amount of the absorbent into the pipette, which is first filled with mercury, connect it by means of a piece of rubber tubing *e* (Fig. 48) with the small burette *f* containing the reagent and supported by the clamp *g*. Open the pinchcock *h*, slip a rubber tube over the burette at *i*, and by suction so exhaust the air in the burette that any gas remaining in the pipette will be drawn through the capillary *x* and through the absorbent. The pipette is thus completely filled with mercury. Stop the suction as soon as the mercury is visible above the rubber *e*, put the rubber tube on the pipette at *l*, and draw the mercury back to the capillary. Note the height of the absorbent in the burette, and then suck the desired amount of the same through the capillary *d* into the pipette. At the moment when the necessary amount of reagent has passed over, bring a drop of mercury into the burette at *i*.

The amount of the absorbent introduced may be sharply determined by drawing the mercury into the pipette until the reagent is again visible in the capillary *d*, and then noting the height of the reagent in the burette.

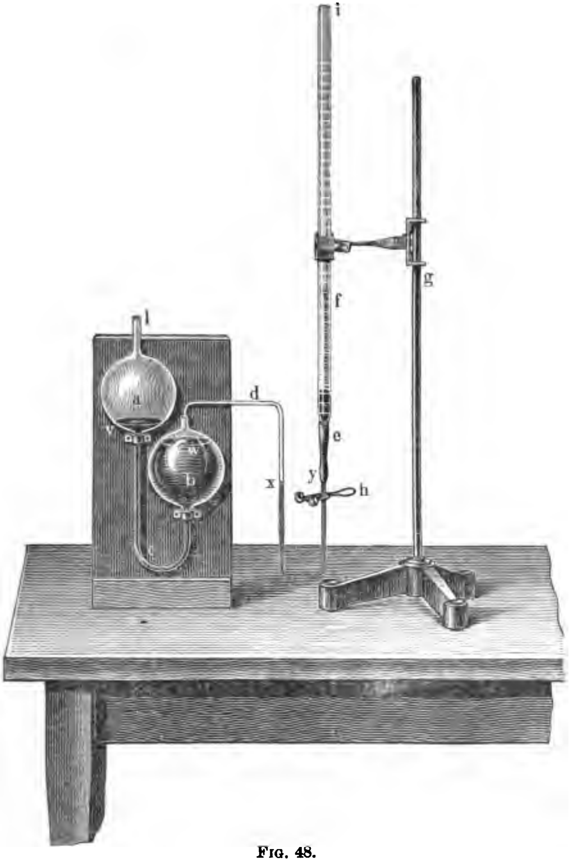

FIG. 48.

The bent capillary tube of the pipette is cleaned and freed from all traces of reagent by lowering the tube into a beaker filled with distilled water, and then drawing water into the capillary and driving it out again by sucking and blowing on a rubber tube attached to the open end of *a*.

The pipette thus prepared for the analysis contains mercury between *v* and *w*, between *w* and *x* the absorbent, and from *x* to *y* mercury.

Gas Pipettes for Solid Absorbents

To bring the gases under examination into contact with solid absorbents, the form of pipette shown in Fig. 49 is used. In this the tube *c* has a branch tube *e* through which solid substances, such as sticks of phosphorus, are introduced into the bulb *b*; *e* is then closed at *f* with a cork, and the pipette is filled as usual with mercury. When a gas is drawn in, the solid substances remain in the bulb *b*, and so come into contact with the gas.

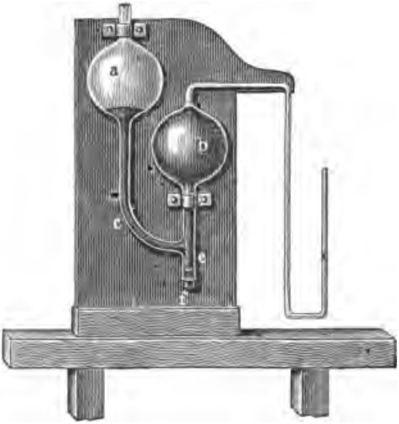

FIG. 49.

THE EXPLOSION PIPETTE

Combustions are made in an explosion pipette (Fig. 50). This has at *f* two platinum wires and at *g* a glass stopcock. The wires are fastened to two screw-eyes, to which are connected the wires from the induction apparatus. To explode a gas mixture, it is brought into the pipette, the stopcock is closed, and into the end of the capillary at *z* a fine sewing needle is inserted, which prevents the mercury being thrown out of the capillary by the strong pressure during the explosion.

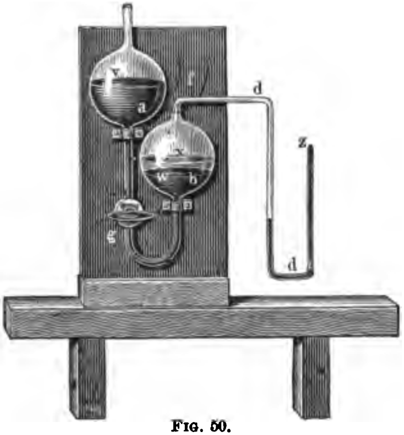

FIG. 50.

THE ABSORPTION

The gas pipettes already described are used for the absorptions, the manipulation being shown in Fig. 51 and Fig. 52.

Figure 51 gives the position in which it is possible to bring the gas completely into the pipette. The measuring bulb is here brought below the surface of the mercury and the gas is drawn into the pipette by sucking with the mouth on a rubber tube attached to *m*. The suction is discontinued at the moment when the mercury begins to flow from the capillary into the bulb of the pipette.

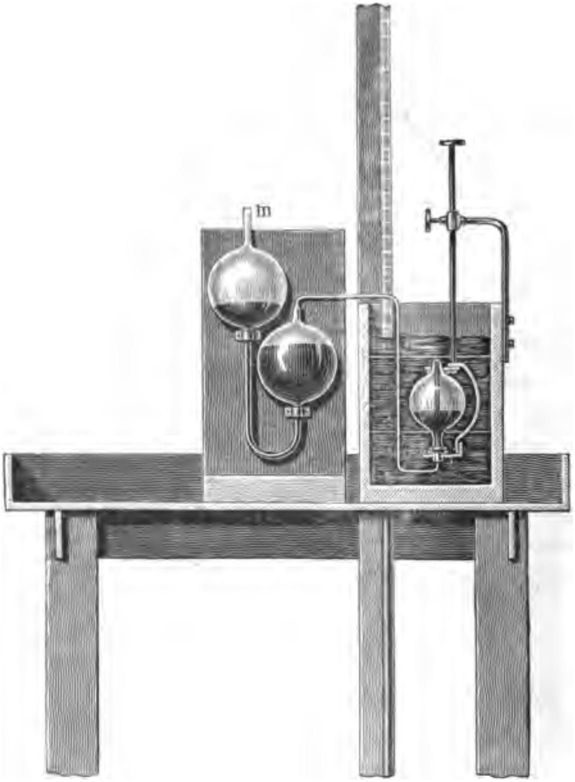

FIG. 51.

The pipette then contains (see Fig. 47) mercury from *v* to *w*, absorbent from *w* to *x*, gas from *x* to *g*, and mercury from *g* to *z*, so that the pipette, after it is taken out of the mercury trough, may be vigorously shaken and a rapid absorption effected.

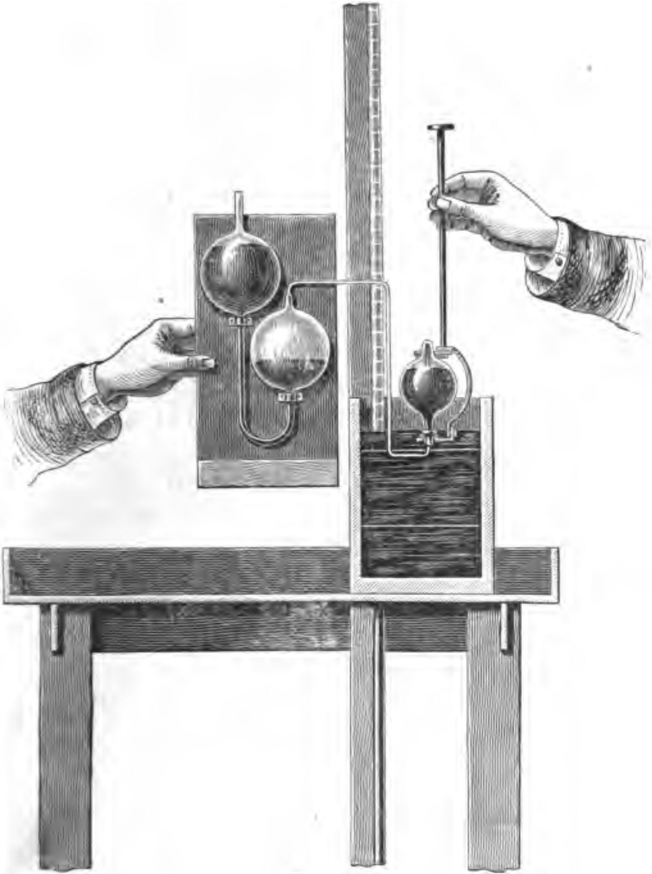

FIG. 52.

To drive the gas from the pipette back again into the measuring bulb, the apparatus is brought into the position shown in Fig. 52.

In the beginning it is necessary to blow into the pipette at *m* to set the gas in motion; when it has once started, the mercury in the measuring bulb acts with an aspirating effect, so that the gas passes over of itself. At the moment when the absorbent has risen to about 1 cm. from the end of the capillary in the measuring bulb, the capillary is lowered under the mercury, and mercury is drawn into the capillary by sucking on the rubber tube attached to *m*. In this manner the entering of reagent into the measuring bulb may be avoided with certainty.

If a gas thread about 1 cm. long remains in the capillary, this corresponds to approximately 0.001 ccm. of gas, since the total 35 cm. length of the capillary has a volume, determined by weighing the mercury which it holds, of 0.038 ccm. Hence from this source no appreciable error arises.

The analysis is made as follows: —

Fill the carefully cleaned and moistened measuring bulb with the gas under examination by lowering the bulb into the mercury in the trough, drawing out the air in it with a gas pipette, and bringing the gas into the bulb either by means of a delivery tube brought under the mouth of the bulb or by means of a gas pipette.

The necessary measurements, absorptions, and explosions now follow, their order being determined by the nature of the gas.

Since difficulties arise only in the use of fuming sulphuric acid over mercury, while all other reagents can easily be manipulated in the manner already described, the reader is referred to the second part of the book for descriptions of the absorptions of the various gases.

The heavy hydrocarbons cannot be absorbed with fuming sulphuric acid in the manner described, because, on bringing together the fuming acid and mercury, sulphur dioxide is evolved even in the cold, and acid sulphates are formed which, upon long standing, separate as thick crusts and obstruct the pipette. Since, however, the gases which are not absorbable by the fuming acid are very insoluble in the same, a pipette completely filled with the acid may be used, the mercury here coming into contact with the sulphuric acid only in the capillary tube. If care be taken in the manipulation that no mercury passes over from the trough into the pipette, and if, after using, all mercury be removed from the capillary by means of a common suction pipette attached thereto, so that sulphuric acid alone remains in the pipette, a stoppage of the capillary, which, when it has once taken place, is difficult of removal, need not be feared.

To protect the lungs from the fumes of the sulphuric acid, a glass tube filled with pieces of caustic potash is interposed between the rubber suction tube and the pipette.

The gases being examined do not here, as in the other absorptions, come in contact with but small amounts of the reagent, hence the errors which might result from the solubility of the gases that are not in an analytical sense absorbable by fuming sulphuric acid could not be disregarded. To obtain an idea of the solubility of the gases in question, illuminating gas was freed from the heavy[1] hydrocarbons and carbon dioxide by absorption, and the residue, consisting of oxygen, carbon monoxide, hydrogen, marsh-gas, and nitrogen, was brought in contact with a large quantity of fresh sulphuric acid.

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[1] By "heavy" hydrocarbons are meant those which are absorbable by fuming sulphuric acid.

The volume of the residue was determined before and after, and it was found that the change in volume could not be measured. Hence the solubility of the gases not absorbable by sulphuric acid may be wholly disregarded.

The data of the experiment were the following: —

About 25 ccm. of illuminating gas was allowed to stand for some time in contact with sulphuric acid, was then freed from sulphur dioxide and the fumes of sulphuric acid by caustic potash, and was measured moist. The result was 757.7 mm. pressure at 16.8° C. The gas was then shaken in a pipette with fresh concentrated sulphuric acid, and after standing for two hours it was brought into the measuring bulb and measured moist. Result — 757.7 mm. at 16.6° C.

The Correction Tube

This tube is used to determine the volume of gas which must be added to or subtracted from the values determined in the analyses, in order to compensate any variations due to changes in temperature or barometric pressure.

The correction tube consists of the glass tube *A*, Fig. 53, the scale tube *B*, and the adjusting tube *C*. To prepare the tube for use, it is placed in the mercury trough of the gas apparatus. The latter should stand in a room where the variations of temperature are but very slight. A very small amount of water is introduced into *A* through *b*, which is as yet open, and mercury is then poured in until it stands at the mark *a* and at the zero mark in the scale tube. The sharp adjustment of the mercury at these heights is effected by sliding up and down in the adjustment tube *C* a glass rod *D*. The rod is joined to *C* by means of a short piece of rubber tubing *c*. When the mercury has been brought to the points mentioned, the upper end of *b* is fused together directly above the water in the mercury trough by means of a small blast-lamp flame. If this is carefully done, there is no appreciable heating of the air volume enclosed in *A*.

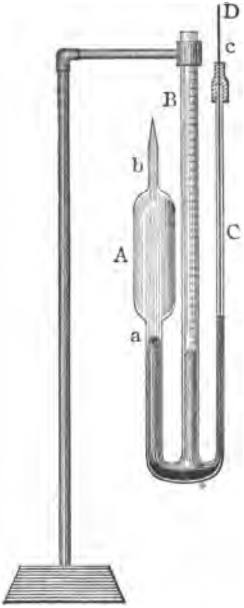

FIG. 58.

The prevailing barometric pressure and the temperature of the water in the mercury trough are now noted so that the volume of air in the apparatus may be calculated. If the barometric pressure changes during the course of the analysis, the influence which this change would have upon the gas pressure in the measuring bulb may easily be determined by placing the correction tube in the mercury trough and bringing the mercury to the mark *a* by raising or lowering the glass rod *D*. The reading on the scale tube *B* then gives the volume which must be added to or subtracted from the values found in the analysis in order to obtain results which are directly comparable with one another.

When a constituent of the gas mixture is to be absorbed with one of the gas pipettes, the correction tube is removed from the mercury trough and is replaced therein before each reading.

Unless very accurate results are desired, it is sufficient to make all readings with the unaided eye, for if the eye be brought only approximately to the same plane with the surface of the mercury column which is to be read, the results thus obtained are quite close to the truth.

The accuracy of the analysis may easily be greatly increased by using a number of measuring bulbs of different sizes and determining their volumes by filling them with mercury and weighing the mercury. The gas to be analysed is then first brought into the largest bulb and one or more of its constituents are determined. If the remaining volume now amounts to only a half or two-thirds of the original volume, this residue is introduced into a smaller measuring bulb. This procedure permits of the use of the total length of the manometer tube *D* (Fig. 43) in making the measurements, and consequently insures much greater 'accuracy in the readings.

CHAPTER V

ARRANGEMENT AND FITTINGS OF THE LABORATORY

THE room for gas analysis should have a northern exposure and should have wide windows. The working-table should run along the outer wall so that the operator may face the window and be able to make his readings without being obliged to turn around toward the source of light. The floor should be mercury-tight, and should slope slightly toward the middle, in order that any mercury that may be spilled may easily be brought together and taken up. If the floor is of wood, it may be made mercury-tight by covering it with canvas or oilcloth, but this covering must then be protected by laying upon it large sheets of cardboard. The room should further be provided with gas and with running water and with a large sink. The sink should have an iron "S" trap, and the lower bend of this trap should be bored, threaded, and provided with a screw plug to permit of the easy removal of any mercury that may collect in the trap.

There should also be an ample supply of water of the temperature of the room. It is convenient to have this water piped to every working-place. This is cheaply accomplished by placing near the top of the room and above the sink a galvanised iron tank containing about 100 liters, and running from the lower part of this tank an iron pipe which passes along the tables. The tank is easily filled through a small iron pipe which hooks over its top and reaches down into the sink, where it may be connected with the faucet by a piece of rubber tubing.

The laboratory should also contain a water suction-pump, a mercury air-pump, a barometer, and accurate thermometers. An electric current is necessary, and this may be supplied either by a battery or storage cells, or the direct current from a dynamo may be utilised. A small induction coil is needed for analyses of gas mixtures by explosion. It is desirable to have narrow shelves fastened to the wall upon which to place the Hempel pipettes.

CHAPTER VI

PURIFICATION OF MERCURY

DISTILLATION IN VACUUM

ONE of the best methods for the purification of mercury is that of distillation as suggested by Weinhold.[1] Unfortunately this does not yield a perfectly pure metal. The author has often found that other metals also distil over in vacuum.

A convenient apparatus for the distillation is that shown in Fig. 54. This corresponds in the main to Weinhold's device, but has some modifications. *A* is a bulb-tube, ground obliquely at the end, and extending to the bottom of the wide tube *D*. Through a stopper in the lower end of *D* is inserted from below a thin glass tube about 1 m. 6 cm. long, which reaches nearly to the bottom of the bulb *A*. The tube *C* is bent as shown in the figure, and has at *a* a side tube with glass stopcock. *D* is connected by a branch tube *b* and a piece of rubber tubing with the level-vessel *J*.

To start the apparatus working, the end of the tube *C* is closed at *c* by a piece of rubber tube and a pinchcock, mercury is poured into *J*, and the apparatus is connected at *a* with a mercury air-pump.

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[1] Carl's *Rep. f. Exp.-Physik*, **15**, 1. Also *Fresenius Zeitschrift f. analyt. Chemie*, **18**, 252.

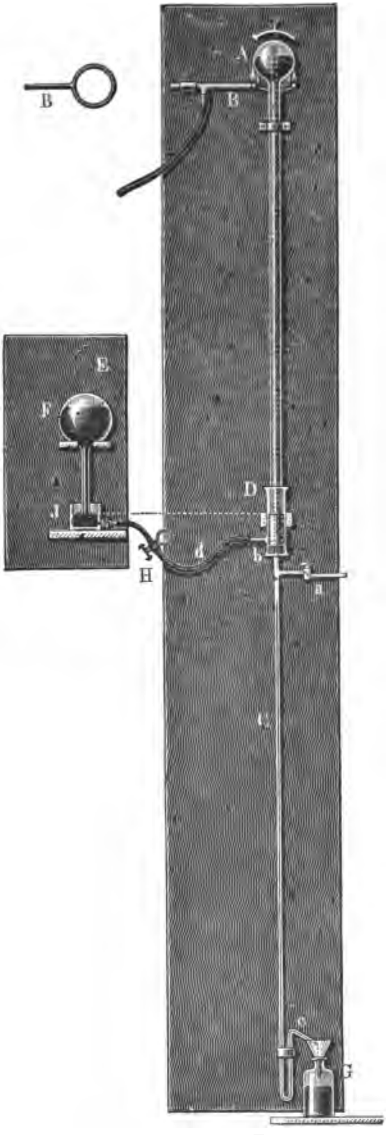

Fig. 54.

As the air is removed from the apparatus, the mercury passes from *J* toward *D* and rises in the space between the tubes *A* and *C*. When the mercury air-pump yields only quite small bubbles of air, the exhausting is discontinued. The level-vessel *J* is now brought into such a position that the mercury, under the prevailing pressure of the atmosphere, fills about $\frac{2}{3}$ of the bulb *A*. To facilitate this adjustment the board *E*, which hangs upon a nail fastened into the wall, has a number of holes bored through it. By inserting the nail through one or another of these holes, the position of the board may easily be changed. If now the bulb is heated by a ring burner, the mercury soon begins to boil, the vapours given off in the vacuum enter the tube *C*, condense there, and after a while the length of the column of mercury which has collected in the tube becomes greater than the height of the barometer. A bottle for receiving the purified mercury is then placed under *C*, and the rubber tube and pinchcock closing *c* are removed. It is advisable to stop the distillation, and after the apparatus has cooled somewhat, to exhaust the apparatus as completely as possible with the mercury air-pump. In this second exhaustion a considerable quantity of air which has been detached from the walls by the heat is always obtained. The apparatus must not be exhausted during the heating, because the mercury may break the whole apparatus by violently boiling when the pressure is decreased.

The ring burner *B* is made from a bent iron tube pierced with little holes, a circle of small, slightly luminous flames being thus obtained. A small screen of asbestos is hung above the bulb to check the upward radiation of heat.

With careful use the apparatus thus arranged may be employed for years, provided that the mercury introduced is always perfectly dry. To effect this the impure mercury is heated in an iron dish to 120°–130° C. The temperature may be easily ascertained by using a thermometer as a stirring rod. The mercury thus dried is poured when cool into the flask *F*, and this is closed with the thumb and inverted in the level-vessel *J*. During this manipulation the connecting rubber tube *d* is closed with the pinchcock *H*.

To distil, the pinchcock *H* is opened, and the apparatus may be left to itself for twelve hours, the height of the mercury in *A* being first adjusted by bringing the board *E* into the proper position.

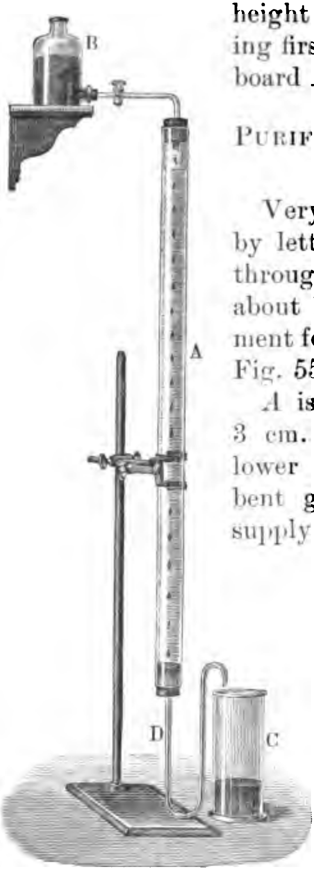

FIG. 55.

PURIFICATION OF MERCURY BY NITRIC ACID

Very pure mercury is obtained by letting it fall in small drops through a column of nitric acid about 1 m. high. The arrangement for this purpose is shown in Fig. 55.

A is a glass tube from 2 to 3 cm. wide, and fitted at the lower end with a cork and the bent glass tube *D*. *B* is the supply bottle for impure mercury, and *C* the receiver for the purified mercury. Some pure mercury is first poured into the tube *D*, and *A* is then filled with dilute nitric acid, the acid being kept in the tube by the pressure of the mercury in *D*. Upon allowing the mercury to drop from *B*, the purified metal passes slowly over into *C*.

PURIFICATION OF MERCURY BY AIR

According to Crafts, mercury is completely purified by leading air through the metal. Leading air through for forty-eight hours suffices for 20 kg. of mercury. Zinc, copper, and lead are completely changed to oxides. The mercury thus purified does not further change upon exposure to the air.

Berzelius had already noticed[1] that foreign substances may be removed from mercury by shaking it with air. Maumené has used the method for the preparation of mercury for barometers. He put 1 kg. of mercury into a liter bottle and fastened the bottle to the wheel of a wagon. After driving for a few minutes, a dust of the foreign metals, mixed with mercury, was formed.

PURIFICATION OF MERCURY BY CONCENTRATED SULPHURIC ACID AND MERCUROUS SULPHATE

This is one of the most convenient of all the methods that have been suggested for the purification of mercury, and it furnishes at once a pure and dry metal.

The process of purification may conveniently be carried out in a heavy separatory funnel of from 2 to 4 liters capacity, the funnel being supported in a wooden stand at such a height that an ordinary bottle or beaker may easily be brought under its lower end. The funnel is first partially filled with mercury (impure mercury may be used here, if no purified mercury is at hand), and then about 500 cc.

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[1] *Chemiker-Zeitung*, 1888, pp. 741, 808. *Ann. de Chim.* **87**, 144.

of concentrated sulphuric acid is poured upon the mercury and from 25 to 50 g. of mercurous sulphate is added. In the top of the separatory funnel is placed an ordinary funnel, the stem of which is drawn out to small diameter and turned upward. The mercury to be purified is poured into this latter funnel and flows slowly and in the form of a fine spray out of the end of the stem. It is freed from foreign metals by the action of the sulphuric acid and mercurous sulphate, and is thoroughly dried by passing through the concentrated acid, so that pure and dry mercury may at any time be drawn off from the separatory funnel. In starting the process, impure mercury which may first have been put into the funnel should, of course, be drawn off and run through

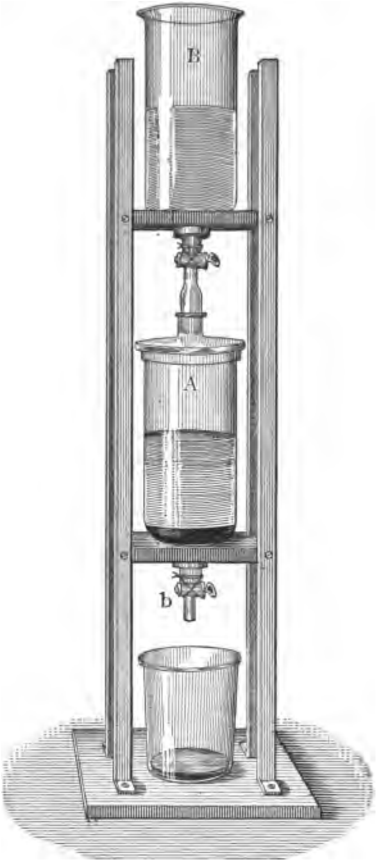

Fig. 56.

the purifier a second time. The mercury in the separatory funnel should never be drawn down until it is near the stopcock, for there might then be danger of drawing off some sulphuric acid with it.

A somewhat more elaborate apparatus for carrying out this purification is shown in Fig. 56. It consists of two bells *A* and *B*, which are closed at the bottom with rubber stoppers provided with glass stopcocks. The upper bell *B* is filled with water, and the lower contains concentrated sulphuric acid and mercurous sulphate. The rubber stopcocks in both of the bells should, of course, always be covered by some mercury. The impure mercury is introduced into *B*, and is then allowed to run slowly from *B* into *A*.

REMARKS UPON THE MAKING OF APPARATUS

In making apparatus, it is a decided mistake to use tubes which are too thick-walled, for such tubes break of themselves, without other cause, upon being exposed to slight changes of temperature. One should further avoid fastening the apparatus at too many places to the wooden or iron standards. As a rule, the glass should be fastened at only a very few points, and even then in such a manner that a free expansion in certain directions is possible. The attachment is best made by fastening a metal band over the glass, but not touching it, and filling the space between the board and the glass with plaster of Paris. If it is necessary to fuse platinum wires in the glass, very fine wire should be used. It is easy to fuse this into the glass absolutely gas-tight without the use of enamel, while thicker wire cannot always be put in perfectly tight even by an expert glass-blower.

CHAPTER VII

ANALYSIS WITH THE USE OF ORDINARY ABSORPTION APPARATUS

GASES which are very easily soluble in water, *e.g.* ammonia, chlorine, sulphur dioxide, etc., are best determined by leading them through a suitable absorption apparatus and ascertaining their amounts by weighing or titration. In doing this it is necessary that the volume of the gases not absorbed be measured by an appropriate apparatus placed either before or behind the absorption apparatus.

This method of analysis is especially well adapted to the determination of very small quantities of a gas.

In analysing a gas mixture by directly determining the volumes of the constituents, all the measurements must be made with the same sharpness; but when the work is done in the manner above mentioned, a much less accurate measurement of the total volume suffices, correct results being obtained if only the determination of the gas in question is accurately made.

For example, in determining the carbon dioxide in the air by measuring its volume, if 100 ccm. of air be taken, the measurements must be exact to the hundredths of a cubic centimeter, even if one wishes only to approximate the accuracy demanded in analyses of the atmosphere. But by using a standardised solution with which the gas is brought into contact, a much greater accuracy may easily be obtained even with relatively rough measurement of the initial volume.

A simple calculation will best make this clear.

Let us suppose that 10 liters of air is taken for the analysis, and that, by titration, 4 ccm. of carbon dioxide is found to be contained therein, *i.e.* 0.04 per cent. Suppose further that a mistake of 10 ccm., which would be an enormous experimental error, has been made in the measurement of the air. The amount of carbon dioxide calculated for an initial volume of 10010 ccm., would be 0.03996 per cent, or for 9990 ccm. 0.04004 per cent.

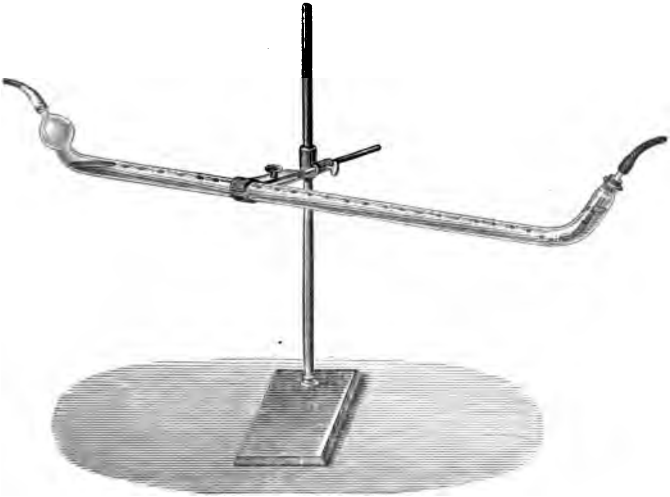

FIG. 57.

Let us suppose further that in using burettes which are graduated in fifths, the error in reading is 0.1 per cent; the above error would then be 2½ times as great as the amount of CO_2 present.

From this it follows that very small quantities of a gas, mixed with large volumes of other gases, should be determined if possible by absorption and subsequent weighing or titration.

A very suitable apparatus for the absorption of gases is the absorption tube proposed by Pettenkofer (Fig. 57), of which a more convenient form has been devised by Winkler (Fig. 58). If gases only are to be absorbed, the Pettenkofer tube is admirably suited to the purpose. If, however, the gases contain substances in the form of dust, a complete absorption is not obtained; in such cases the gas bubbles must be broken up, this being done by means of a long perpendicular glass tube filled with glass beads. A convenient device for this purpose is a combination of such a tube with a Peligot tube (Fig. 59).

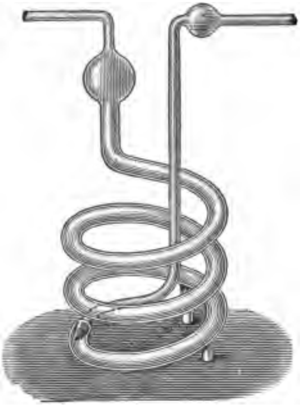
Fig. 58.

If the vessel may be shaken during the absorption, a simple Woulf bottle answers every purpose.

To absorb large amounts of gases the apparatus devised by Winkler may advantageously be used. He obtains a large surface of contact by employing light and porous pumice-stone, and the absorption apparatus he uses has the form shown in Fig. 60. The cylinder *a* has two openings at the top, and it ends at the bottom in a tube which is ground into the neck of the Woulf bottle *b*. The bottle contains the absorbing liquid, and *a* is filled with pieces of pumice-stone. Upon blowing into *d* the liquid is made to rise, the pumice-stone becoming thereby thoroughly moistened. Upon reopening *d* the excess of liquid flows back into *b*, and the apparatus is ready for the absorption. The gas enters through the tube *c*, which extends as far as the narrow part of *a*, and then rising through the moistened pumice-stone it passes out at *e*.

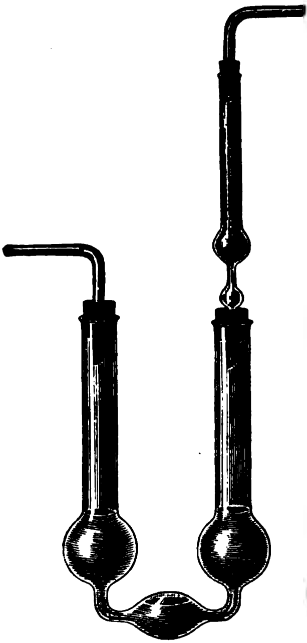

FIG. 59.

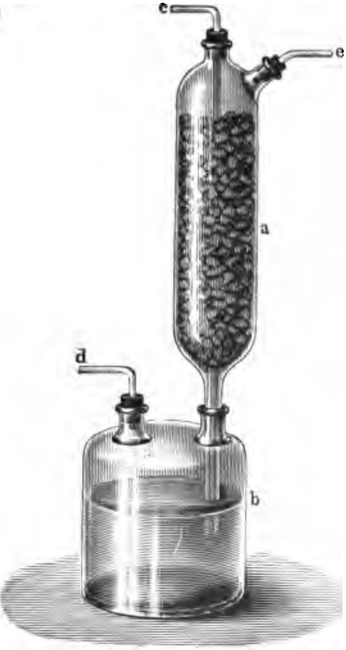

FIG. 60.

Reiset[1] has constructed a very effective absorption apparatus for the determination of carbon dioxide in the atmosphere, this device rendering it possible to work with very large volumes of air (600 liters). The construction is shown in Fig. 61. *I* is a U-tube filled with pieces of pumice-stone moistened with concentrated sulphuric acid. At the lower end of the tube is a bulb in which collects the dilute sulphuric acid that would otherwise retard the passage of the air. This tube *I* acts as a drying tube; it holds back the total moisture of the air used in the experiment, and its increase of weight gives the percentage of moisture in the air. The dried gas now passes into the absorption apparatus proper through the tube *t*

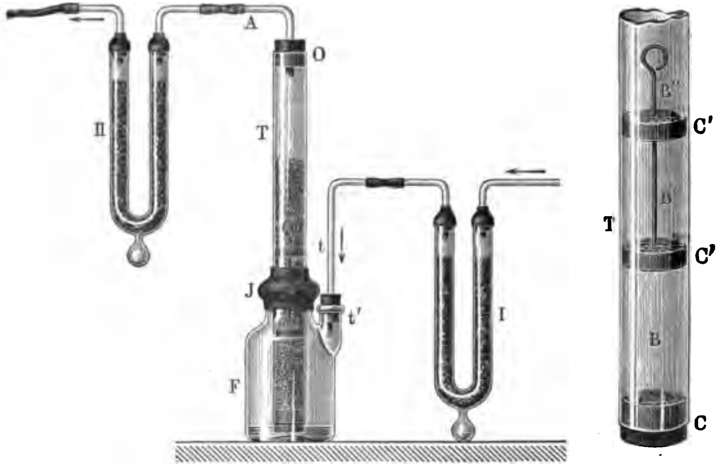

Fig. 61.

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[1] *Comptes rendus*, **88**, 1007; and **90**, 144. *Chemiker-Zeitung*, **4**, 485.

which is fastened into the neck of the bottle *F*. This part of the apparatus is based upon the principle which Schlösing made use of to absorb the ammonia in the atmosphere, and to facilitate its quantitative determination. Three slightly conical little boxes, *C*, *C′*, and *C″* (Fig. 61), made from thin platinum foil, are pushed into the glass cylinder *T*, the friction with the sides of the tube holding them in place. Each little box has a diameter of 4 cm., and is pierced with 120 holes of about 0.5 mm. diameter. *T* is 0.5 m. long. It is joined to *F* by means of a thick, tightly fitting rubber ring *J*. Before beginning the analysis 300 ccm. of a clear standardised solution of baryta water is put in the tube. The tube is then connected air-tight with the U-tube *II*, which is filled in exactly the same manner as *I*, and the aspirating is begun.

At the end of the experiment, that is, after 600 liters of air had passed through, Reiset found the baryta water in the bottle and in the lowest part *B* of the cylinder completely charged with carbonate, that in *B′* only milky, while the solution in *B″* was clear and transparent — a proof that the carbon dioxide was completely absorbed.

The baryta water is now brought into a bottle supplied with a tightly fitting stopper, and the cylinder and bottle are carefully rinsed with known quantities of water.

The U-tube *II* is weighed, and the amount of water carried over from the baryta water is thus determined. The barium carbonate is allowed to settle, and as the total amount of liquid is now known, a titration of a measured portion of the clear solution gives the amount of unchanged barium hydroxide, and, by a simple calculation, the per cent of carbon dioxide in the atmosphere. (The measured volume of air is of course always reduced to 0° and 760 mm. pressure).

For measuring gases a gas-meter or simple aspirator is employed. The measurement can be made very simply by calculating the gas volume from the amount of water which has flowed from the aspirator, with corrections for temperature and barometric pressure.

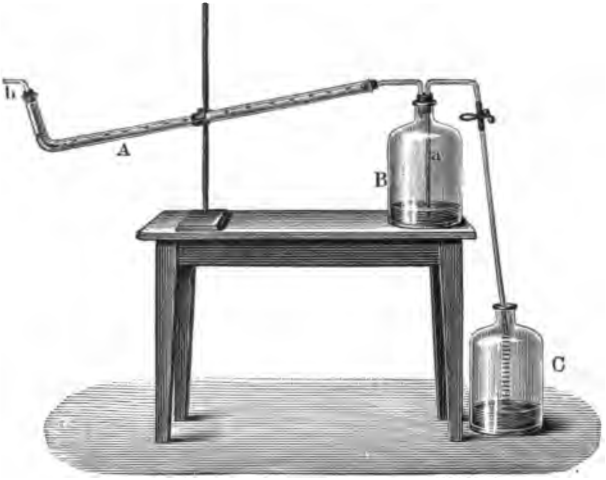

FIG. 62.

Figure 62 shows such an arrangement. *A* is a Pettenkofer tube, *B* is a bottle which can be emptied by the glass siphon *a*, *C* is a graduated bottle. To make a determination, bring an accurately measured amount of reagent into the absorption tube, open the siphon, and measure the quantity of water which passes over, beginning the measurement at that moment when the first bubble passes from *b* into the absorbing liquid.

PART II

SPECIAL METHODS

CHAPTER I

GENERAL REMARKS UPON ABSORPTION ANALYSES WITH THE APPARATUS FOR TECHNICAL GAS ANALYSIS

THE accuracy which may be attained by simple absorptions carried out in the apparatus previously described is so great, even when the analyses are made over aqueous solutions, that it is but slightly inferior to the exact analyses made over mercury, and in all cases completely satisfies the demands made upon the technical chemist.

For the sake of comparison, two partial analyses by this method and an exact analysis over mercury (see Part I. Chap. IV. *B*) are here given; the gas used in each case is illuminating gas, taken September 23, 1877.

I. Technical Analysis	II. Technical Analysis	Exact Analysis over Mercury	
1.6 per cent	1.5 per cent	1.5 per cent	carbon dioxide
3.1 "	2.9 "	3.0 "	heavy hydrocarbons
1.4 "	1.6 "	1.4 "	oxygen.

Errors so large that they may entirely destroy the value of the analysis result when the apparatus and the reagents do not have the temperature of the laboratory, or when the temperature changes during the brief time necessary for the analysis. Since, for example, a rise of temperature of only one degree would cause an error of 0.3 per cent in a total volume of 100 ccm., it follows that working near a stove, boiler, fire, etc., is wholly inadmissible, and that the apparatus and confining liquids must be kept at the place where the analysis is made.

It is of no less importance for the obtaining of accurate results that the confining liquids be allowed to flow down from the walls of the burette in exactly the same manner after each absorption. Otherwise an error may be caused by the adhering of more or less liquid to the glass walls. One can easily convince himself by experiment that, with gases confined over water, readings which are made one minute after the gas has been shaken with water in the burette differ by several tenths of a cubic centimeter from readings made five minutes later. With all other liquids, such as caustic alkalies, cuprous chloride, concentrated sulphuric acid, etc., the running-down takes place much more slowly, so that an error of one cubic centimeter or more may result. The condition of the glass plays an important part here, as in all adhesion phenomena. An invisible layer of salt or fat acts, of course, quite differently from the clear glass surface.

The author has found by repeated experiment that distilled water will run down completely in five minutes, while a five per cent solution of sodium hydroxide requires ten minutes, and concentrated sulphuric acid from fifteen to twenty. For this reason, rapid and at the same time accurate work is quite impossible in all those forms of apparatus in which the gas is not always measured over the same liquid.

In the method previously given, the gases pass from the pipettes into the measuring burette in nearly equal periods of time, or in time proportional to the volume of the gases, since the connecting capillary acts as a regulator, and also since the adhesion of the water in the burette does not vary during the analysis. For these reasons the reading may be taken either shortly after the gas has been drawn back into the burette, or after the water has run down, and good results may be obtained in both cases. The most accurate results are naturally obtained from readings taken after the water has run down completely.

Confirmatory Analyses

Partial analysis of a sample of illuminating gas taken September 13, 1877.

I. 100 ccm. of gas were taken.

The readings were made five minutes after passing the gas back into the measuring burette; that is, after complete running down of the water.

Results —

2.4	per cent	carbon dioxide
3.4	"	heavy hydrocarbons
0.8	"	oxygen
8.1	"	carbon monoxide.

II. The readings were made one minute after passing the gas back, the running down of the water not being waited for.

Beginning of the analysis, 10.36 A.M.
End " " 11.14 "

Results —

2.0 per cent carbon dioxide
3.3 " heavy hydrocarbons
0.7 " oxygen
8.1 " carbon monoxide.

CHAPTER II

CONCERNING THE SOLUBILITY OF GASES IN THE ABSORBENTS

THERE is no doubt that working with unsaturated absorbing liquids leads to the most erroneous results, and that on account of the variation of temperature and pressure the highest scientific accuracy can be attained only by working over mercury and with solid absorbents. In by far the greater number of cases, however, the use of aqueous solutions is possible if they are allowed to become saturated in the manner mentioned on p. 53.

It would be a decided mistake if, for example, in an analysis of a mixture of carbon dioxide, nitrous oxide, and nitrogen, the absorbing liquid were saturated with nitrous oxide by leading the pure gas through the absorbent, and thus bringing it into contact with the liquid at the pressure of an atmosphere. The error, however, is very small if the absorbent is saturated in such a manner that the amounts of dissolved gases correspond exactly to the partial pressure which the various constituents will exert in the analysis to be made. Although this may not be possible in a theoretical sense, yet in most cases it may be accomplished to a quite sufficient degree by making, with the same absorbent, two or three analyses of the same gas mixture, one directly after another. It is precisely this consideration which gives the great exactness to the work with the pipettes devised by the author, an exactness that cannot be attained with the simple gas burettes. In the examination of industrial gases, where repeated analyses of nearly identical gas mixtures are made, the pipettes remain of themselves sufficiently saturated, so that a double analysis is generally unnecessary. Parallel analyses, made by the author, over water on the one hand and over mercury on the other, serve to confirm the statement given above.

The determination of carbon monoxide in a gas gave —

With unsaturated reagent —

8.6 and 8.5 per cent.

With saturated reagent —

8.1 and 8.0 per cent.

Two partial analyses of a sample of illuminating gas taken April 24, 1879, gave —

With unsaturated confining water —

3.5	per cent	carbon dioxide
4.6	"	heavy hydrocarbons
11.2	"	carbon monoxide.

With saturated confining water —

3.3	per cent	carbon dioxide
4.6	"	heavy hydrocarbons
10.3	"	carbon monoxide.

Washing out the reagents from the burette with water, as several writers have proposed, is thus quite impracticable, as one may easily convince himself by comparing results so obtained with those given by an exact analysis.

If an analysis need be accurate only to within 0.5 per cent, it is unnecessary to first saturate the confining water with the gas under examination.

Errors much larger than those mentioned above — so large, in fact, as to give completely misleading results — arise from faulty arrangement of the apparatus in taking the sample.

CHAPTER III

CONCERNING THE COMBUSTION OF GASES

SINCE absorbents for all gases are not as yet known, the combustion of certain inflammable gases is an operation of great importance.

The heating of the gases to the temperature of combustion from within the mixture is accomplished either by an electric spark, the combustion then taking place in an instant as an explosion, or by means of an electrically heated platinum spiral which is brought to glowing in the gas mixture.

The gas can also be heated from without by leading it through a tube of glass or platinum which is heated to glowing by a flame.

By means of the combustion, the nature and volume of the elementary constituents of a single combustible gas of unknown composition and its molecular structure may be determined.

Bunsen has stated the theoretical data in his *Gasometrische Methoden*, 2d ed., 1877, pp. 48–51.

If, in this question, we start with the most complicated case, viz., that in a volume of a gas there are x vol. of gaseous carbon, y vol. hydrogen, z vol. oxygen, and n vol. nitrogen, then four equations are necessary for determining x, y, z, and n. To obtain these four equations it suffices to burn a volume V of the gas in question, and then to determine (1) the contraction C resulting from the combustion; (2) the aqueous vapour Y which has been formed; (3) the resulting carbon dioxide X; and (4) the separated nitrogen S.

The gaseous carbon x contained in a unit volume of the gas gives $2x$ carbon dioxide, and V volumes give $2x\mathrm{V}$. Hence

$$\mathrm{X} = 2x\mathrm{V}, \quad \text{or} \quad x = \frac{\mathrm{X}}{2\,\mathrm{V}}.$$

The hydrogen y contained in one volume of the gas gives y volumes of aqueous vapour, V volumes give $\mathrm{V}y$. Hence

$$\mathrm{Y} = y\mathrm{V}, \quad \text{or} \quad y = \frac{\mathrm{Y}}{\mathrm{V}}.$$

Since, further, in a unit volume of the gas there are n volumes of nitrogen, and in V volumes $\mathrm{V}n$ nitrogen, it follows that

$$\mathrm{S} = \mathrm{V}n, \quad \text{or} \quad n = \frac{\mathrm{S}}{\mathrm{V}}.$$

Finally the volume of gas before the combustion is made up of the gas volume V and the oxygen volume O which has been added. The gas volume remaining after the combustion is equal to the oxygen volume O added, minus the oxygen volume $2x$ necessary to the formation of the carbon dioxide, minus the oxygen volume $\frac{1}{2}y$ necessary for the formation of the water, plus the volume of the carbon dioxide formed $2x$, plus the oxygen volume z contained in the original gas, plus the nitrogen volume n separated from the gases by the combustion. Substituting now the values found for x, y, and n, we have —

As volume before the combustion, $V + O$;

As volume after the combustion, $O - \frac{Y}{2V} + z + \frac{S}{V}$.

Subtracting the lower expression from the upper, there results, for the gas volume which has disappeared —

$$C = V + \frac{Y}{2V} - z - \frac{S}{V},$$

or $$z = V - C + \frac{Y}{2V} - \frac{S}{V}.$$

To determine V, X, Y, S, and C by experiment, V volumes of the gas under examination are brought into the explosion eudiometer, an amount of oxygen O necessary for the combustion is added, and the mixture then ignited. The reduced gas volume disappearing in the explosion is C.

The eudiometer is now heated to 100° C. in a suitable apparatus. The difference between the reduced volumes before and after the heating is Y.

The volume of carbon dioxide X is next determined by means of a potash ball. The residue now in the eudiometer consists of nitrogen mixed with an unknown amount of oxygen. This latter is determined by combustion with hydrogen, and is subtracted, and the volume of nitrogen is thus found.

If chemical tests show that the gas contains no oxygen, *i.e.* that $z = 0$, then

$$0 = V - C + \frac{Y}{2V} - \frac{S}{V};$$

substituting the value Vy for Y, there results —

$$0 = V + \frac{y}{2} - C - \frac{S}{V}, \quad \text{or} \quad y = 2\left(C + \frac{S}{V} - V\right).$$

With the aid of this equation the hydrogen contained in a unit volume of a gas free from oxygen may be calculated from the contraction, the direct determination of the volume of aqueous vapour Y being thus rendered unnecessary.

The method holds good for nitrogen, oxygen, hydrogen, and all gases of the following composition: —

n vol. C + n_1 vol. N = 1 vol.
n " C + n_1 " O = 1 "
n " C + n_1 " H = 1 "
n " H + n_1 " = O 1 "
n " H + n_1 " N = 1 "
n " N + n_1 " O = 1 "

n vol. C + n_1 vol. H + n_2 vol. O = 1 vol.
n " C + n_1 " H + n_2 " N = 1 "
n " H + n_1 " O + n_2 " N = 1 "
n " C + n_1 " O + n_2 " N = 1 "
n " C + n_1 " H + n_2 " O + n_3 " N = 1 vol.

It is seen that in this list of gases there are some, namely O and n vol. N + n_1 vol. O = 1 vol., which contain no constituent combustible with oxygen. With such gases hydrogen must be added for the combustion instead of oxygen. If V is the initial volume, C the gas volume disappearing in the combustion, and H the hydrogen added, we then have as —

Vol. before the combustion

$$(1)\ V + H,$$

and after the combustion the volume will be —

The hydrogen added, minus twice the volume of the oxygen in the gas, plus the remaining nitrogen, or

$$(2)\ H - 2z + n.$$

Subtracting (2) from (1) we get

$$C = V + 2z - n,$$

or

$$z = \frac{C - V + n}{2}.$$

It is thus possible on the one hand to determine the molecular constitution of a gas by combustion, while, on the other hand, the quantitative proportions of the various constituents of a gas mixture whose qualitative composition is already known, can, of course, be ascertained by combustion.

By experiment can be determined —

1. The total contraction caused by the burning of the gases.
2. The water formed in the combustion.
3. The carbon dioxide formed in the combustion.
4. The oxygen used in the combustion.
5. The nitrogen remaining after the combustion.

Five equations may be made from these experimental figures thus derived and from the known combustion relations of the gases; hence, by means of a single combustion of a gas mixture containing five different gases which are qualitatively known, the amounts of these five gases may be determined.

Since we can sharply separate most gases by means of absorbents, the combustion is generally used only for the separation of nitrogen from hydrogen, marsh-gas, and the higher members of the marsh-gas series.

Of especial significance is Bunsen's discovery that nitrogen and oxygen, in very violent explosions, combine directly to form nitric oxide or nitrogen tetroxide and nitric acid. Bunsen found that —

100 vol. of air with 13.45 oxyhydrogen would not burn.

						Vol. of Air remaining
100	air	burned with	26.26	oxyhydrogen	gas, left	100.02
100	“	“	34.66	“	“	100.15
100	“	“	43.72	“	“	100.07
100	“	“	51.12	“	“	99.98
100	“	“	64.31	“	“	99.90
100	“	“	78.76	“	“	99.43
100	“	“	97.84	“	“	96.92
100	“	“	226.04	“	“	88.56

Bunsen seeks to avoid the inaccuracies which exist in many of the older gasometric results by never using in his experiments more than 26 to 64 volumes of combustible gas to 100 volumes of incombustible gas.

These figures give us undoubtedly a sharp dividing line, but the author would call attention to the fact that they do not hold good in all cases. The author has ascertained by experiment that the explosion phenomena, when marsh-gas and oxygen or carbon monoxide and oxygen are used, are quite different, and call for different proportions of gas.

The gases named give less violent explosions. By following Bunsen's directions it is possible that the gas mixture may not at times be sufficiently explosive, but it has long been supposed that under the conditions which he laid down, the burning of any nitrogen present would always be avoided. According to L. Ilosvay,[1] however, the union of nitrogen and oxygen takes place in the flame of the Bunsen burner even when carbon dioxide is introduced into the flame to lower its temperature, and he states that oxides of nitrogen are also formed when air burns in an atmosphere of illuminating gas. A. H. White[2] states that oxides of nitrogen are always formed in explosion analyses in amount increasing with the violence of the explosion.

By practice one very quickly learns to judge from the appearance of the flame caused by the explosion as to whether the explosion has been strong enough. For complete combustion it is necessary that an active explosion take place. In incomplete combustion the progress of the flame in the gas mixture can be followed by the eye.

Every combustible gas when mixed with air is inflammable only within certain limits.* The following percentages of gases when present in a mixture with air will burn: —

5	to 13	per cent	CH_4
3	" 82	"	C_2H_2
4	" 22	"	C_2H_4
5	" 72	"	H

---

[1] *Bull. Soc. Chim.*, 1889, p. 737.
[2] *J. Am. Chem. Soc.*, **23**, 476.

13	to 75	per cent	CO
9	" 55	"	water gas
5	" 28	"	illuminating gas
6	" 13.4	"	oil gas
.4	" 15.5	"	mixed gas containing 25 per cent C_2H_2 and 75 " oil gas
11.9	to 28.5	"	COS.

If larger amounts of gas are available, they may be burned by mixing them with air or with oxygen, leading them over heated copper oxide, and weighing the carbon dioxide and water formed. R. Fresenius suggests[1] the use of a combustion tube about 30 cm. long and not too wide, filled, without a canal, with coarse-grained copper oxide. The copper oxide is held closely together by means of stoppers of asbestos, about 7 cm. long, inserted in each end of the tube. The asbestos must first be ignited in moist and then in dry air. The tube is wrapped with wire gauze, and is heated to red heat in a small combustion furnace. The gas and the air or oxygen necessary for the combustion are led over soda-lime or calcium chloride, and it is best to bring them together after they have entered the combustion tube, the gases entering the tube separately through the two openings of a rubber stopper. The gas must previously be accurately measured. The water formed in the combustion is absorbed in a calcium chloride tube, and the carbon dioxide in a Liebig potash bulb.

The combustion may be made in a much simpler manner by explosion in pipettes.

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[1] *Zeitschrift für analytische Chemie*, **3**, 339.

The Explosion Pipette for Technical Gas Analysis (Fig. 63)

This consists of the thick-walled explosion-bulb *a* and the level-bulb *b*, which are joined together by a wrapped piece of rubber tubing. At *c* two fine platinum wires are fused into the explosion pipette, the ends of the wires being about 2 mm. apart. At *d* is a glass stopcock, and the pipette terminates in the capillary *e*, whose end is closed by a short piece of rubber tubing and a pinchcock. In general, the pipettes and burettes for technical gas analysis are filled with aqueous solutions, but the explosion pipette is filled with mercury. By using mercury as confining liquid during the explosion it is possible afterward to determine the carbon dioxide formed in

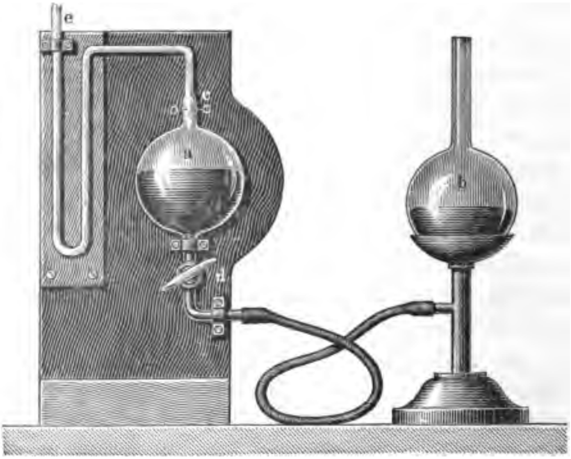

Fig. 63.

the combustion. If the explosion is made over water, a subsequent measuring of the carbon dioxide formed is inadmissible, because the pressure in the pipette is so high during the explosion that considerable quantities of carbon dioxide are absorbed by the water. By exploding over mercury very satisfactory results are obtained, even if the carbon dioxide is afterward measured in a burette which is filled with water.

One is often called upon to analyse gas mixtures which do not contain sufficient combustible ingredients to make them explosive when mixed with oxygen or air; in such cases combustibility is produced by adding pure hydrogen.

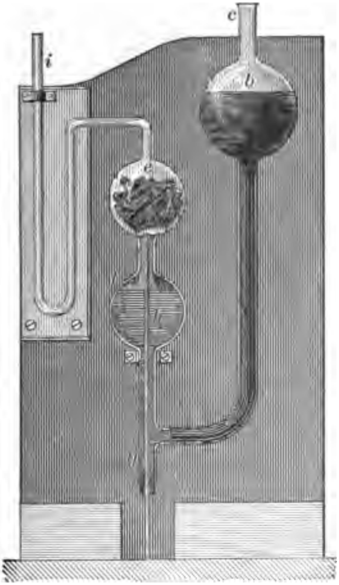

FIG. 64.

The hydrogen is made in the hydrogen pipette (Fig. 64). This is a simple absorption pipette which has two bulbs in the place of the first large bulb. Through the tube *g* a glass rod *h* is pushed up to the mouth of *e*. This rod is fastened tightly into *g* by means of a piece of rubber tube slipped over it, and it serves to hold pieces of chemically pure zinc in the bulb *e*. To fill the pipette it is inverted, the glass rod is taken out, and the pieces of zinc are dropped into *e*. The pipette is then closed again, placed upright, and filled with diluted sulphuric acid (1.10) by means of a funnel. The pipette is closed at *i* with a piece of rubber tubing and a pinchcock.

After a short time the hydrogen produced will drive back the acid, so that the evolution ceases. Before drawing off the sample of hydrogen from the pipette it is advisable to connect with the capillary *i* a gas burette, and to draw off the gas in the pipette until the bulb *e* is completely filled with sulphuric acid. A new supply of pure hydrogen is now generated, and this gas may be used in the analysis. If several analyses are made one after another, this fresh evolution of the gas is unnecessary; but if the apparatus has stood for any length of time, air will diffuse through the sulphuric acid, and some oxygen and nitrogen will be found in the first portion of hydrogen that is drawn off. To obtain a more active evolution of hydrogen than that which takes place when pure zinc and pure acid are used, a few pieces of platinum foil may be put in with the zinc.

THE EXPLOSION PIPETTE FOR THE APPARATUS FOR EXACT ANALYSIS (FIG. 65)

In the exact analysis also it is most convenient to make the explosions in a pipette especially constructed for the purpose. This pipette differs from the ordinary pipettes only in having a stopcock at *a* and two platinum wires fused in at *b*.

To burn a gas mixture in this apparatus, the gas is brought into it in the usual manner, the stopcock is closed, and a fine sewing needle is placed in the mouth of the capillary *c*. Upon connecting the platinum wires with an induction apparatus, the mixture is exploded by the spark which passes when the circuit is closed.

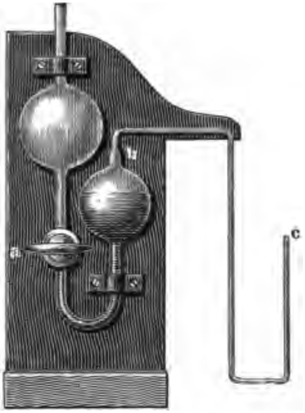

FIG. 65.

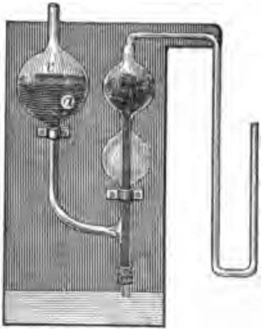

FIG. 66.

Hydrogen is made in the

HYDROGEN PIPETTE (FIG. 66)

the construction of this pipette resembling that of the hydrogen pipette shown and described on page 131.

The most suitable apparatus for the evolution of oxyhydrogen gas is one closely resembling the Bunsen apparatus.

THE OXYHYDROGEN GAS GENERATOR

The author has found that in the evolution of oxyhydrogen gas there is always formed some ozone, which upon being passed through mercury unites with the metal. For this reason oxyhydrogen gas, in which the ozone has not been previously decomposed, leaves a slight residue of hydrogen when one works over mercury. If the oxyhydrogen gas is collected over potassium iodide, iodine is set free even after the evolution has proceeded for some hours. A direct experiment gave 0.7 ccm. of free hydrogen in a liter of the gas. The ozone is removed either by putting the apparatus, during the evolution, into water heated to 90°, or by exposing the oxyhydrogen gas, before using it, to the action of diffused daylight for 12 hours, whereby the ozone disappears of itself. The latter way is the more convenient, and hence in the apparatus, Fig. 67, the bulb *c* of about 50 ccm. capacity is interposed between the delivery tube *b* and the vessel *a*. When the apparatus is put into use, it is filled by a rapid evolution of oxyhydrogen

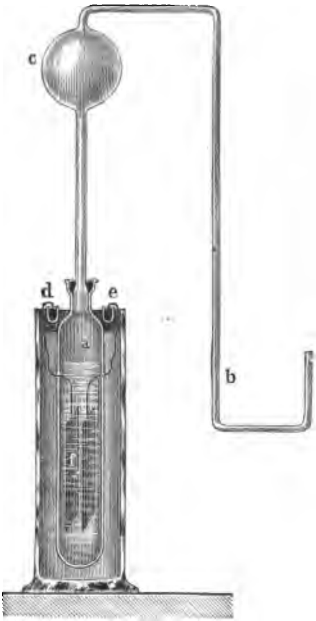

FIG. 67.

gas lasting for 1½ hours, and is then allowed to stand for 12 hours. If inside of 24 hours never more than 40 ccm. of the gas be taken for analysis, one may be sure that only pure oxyhydrogen gas is being employed. To take off a portion of the gas, the delivery tube is brought into the measuring bulb, and by further evolution of the oxyhydrogen gas the desired amount of the same is driven over. The freshly evolved gas containing ozone drives the pure gas before it. Two little glass cups, *d* and *e*, serve as pole contacts. The gas is set free by the plates *f*. A little mercury in the delivery tube at *b* closes the apparatus air-tight.

THE DIP BATTERY

For producing the electric current, the form of dip battery devised by Bunsen is very convenient (Fig. 68).

In this form the zinc and carbon plates stand opposite one another, and are dipped into a single solution which is prepared as follows:[1] 765 g. of commercial pulverised potassium bichromate, which usually contains about 3 per cent of impurities, is gradually brought into 0.832 liter of sulphuric acid of 1.836 sp. gr., the acid being constantly stirred. When the potassium bichromate has been changed to chromic acid and potassium sulphate, 9.2 liters of water is poured in, in a thin stream, with constant stirring. The mixture, which was already hot, now heats up still more, and the crystals gradually dissolve.

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[1] Poggendorff's *Annalen*, 1875, **154**, 248.

The above amounts make 10 liters of the battery solution.

If the circuit be closed by a conductor of low resistance, there may be seen in the red solution a dark-coloured column of liquid which, starting from the dissolving zinc plate, sinks to the bottom and collects in the lower part of the glass cell in the form of a rather sharply defined layer.

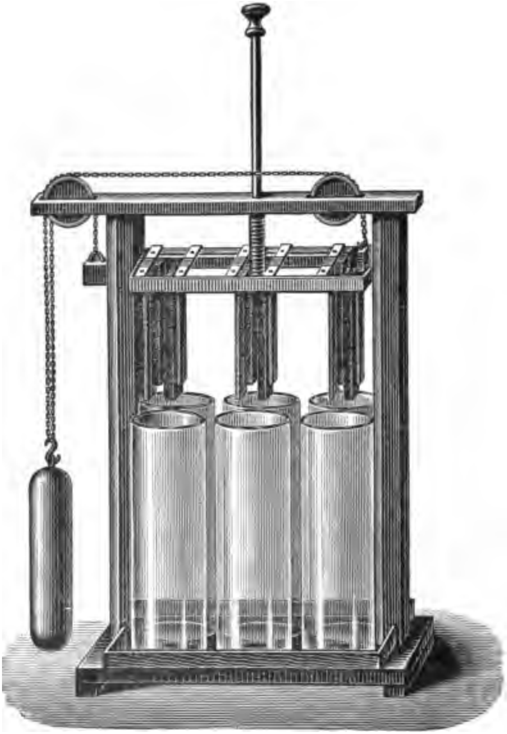

Fig. 68.

The original solution has a specific gravity of 1.140, while that charged with the zinc sulphate has a specific gravity of 1.272. Hence the liquid once used sinks to the bottom and is constantly replaced by fresh, unchanged solution. A circulation is thus established which has a considerable influence upon the constancy of the current.

THE INDUCTION COIL

Sparks for the explosion are best obtained by means of a Ruhmkorff inductor. Too small a coil should not be chosen, but one about 15 cm. long will be found sufficient. If the induction coil is too small, it may easily occur that the spark is too weak to ignite a gas mixture which is but slightly explosive.

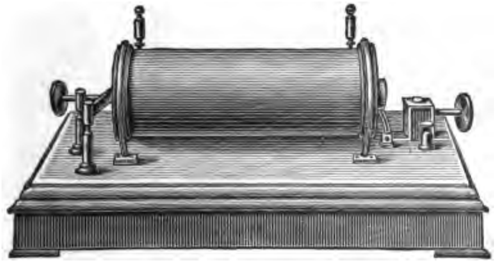
FIG. 69.

The author would further recommend, even though in hundreds of analyses he has never known an explosion pipette to burst, that the instrument be placed behind a screen of plate glass before making the explosion, so that the experimenter may surely be protected against accident.

THE COMBUSTION WITH AN ELECTRICALLY HEATED PLATINUM SPIRAL

J. Coquillion was the first to propose the use of the glowing platinum spiral in the determination of such gases as marsh-gas and hydrogen. Clemens Winkler improved the form of the apparatus and used a Hempel pipette for solid and liquid reagents, Fig. 32. While adhering for the most part to the Winkler arrangement, L. M. Dennis has lately further improved the apparatus so far as the process of combustion is concerned, by arranging it for use with mercury corresponding to the mercury pipettes already described. The apparatus is shown in Fig. 70.

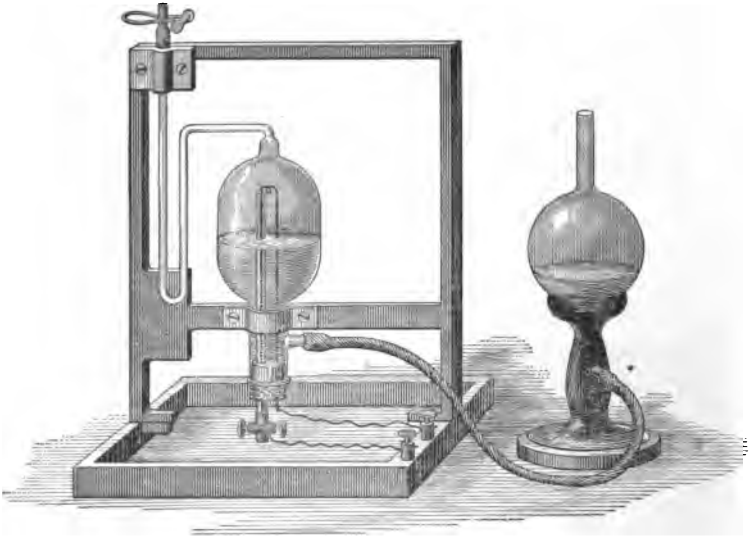

FIG. 70.

In the neck of the pipette is inserted a single bore rubber stopper. A glass tube reaching nearly to the top of the pipette passes through the opening of the stopper. Inside of the glass tube is a stout iron wire which projects below its lower end. The joint between the glass tube and the iron wire is made air-tight by slipping a short piece of thick-walled rubber tubing over both and wiring it in place. Another piece of stout iron wire is pushed up through the stopper so that it occupies the position shown in the figure. The upper ends of these wires are joined by a spiral of platinum wire $\frac{1}{4}$ mm. in diameter, the coil of the wire being about 2 mm. in diameter and containing from 20 to 30 turns. This spiral is bent into the form of a horizontal S. The lower ends of the two iron wires are joined to two insulated binding posts, as shown in the illustration.

After the rubber stopper has been inserted in place, and the wires have been connected with the binding posts, the pipette and capillary are filled with mercury by raising the level-bulb. The pinchcock on the rubber tube on the capillary is closed and the tube of the level-bulb is connected with a water suction pump. By applying suction in this manner the air in the glass tube surrounding the one iron wire is drawn out and rises to the top of the pipette, the tube becoming completely filled with mercury.

Winkler mixed with air the gas which is to be burned and then allowed this mixture to flow slowly through a burette into the combustion pipette against the glowing platinum spiral. Dennis, on the other hand, brings into the pipette the total amount of the gas which is to be burned, and then introduces into the burette a volume of *oxygen* which is more than sufficient for the combustion, and notes this volume. He then joins the burette with the pipette in the usual manner by means of a bent capillary tube, heats the platinum spiral to glowing, and then with the spiral still glowing slowly passes oxygen over into the combustion pipette. The chief advantages of this procedure are: first, the use of a large volume of combustible gas and consequent increase in the accuracy of the work; second, the avoidance of explosion by the *gradual* addition of oxygen; and third, the avoidance of the formation of oxides of nitrogen in the combustion of all such gas mixtures as contain little or none of this gas because of the addition of pure oxygen instead of air.

THE COMBUSTION WITH A PLATINUM CAPILLARY TUBE

The two methods just described necessitate the use of an electric current. The combustion can also be effected by means of a platinum capillary tube heated from without with a flame, provided that this flame generates only just enough heat to bring the capillary to glowing. Orsat had already stated that it must be possible to burn methane by means of a heated capillary platinum tube, but the actual solution of this problem is original with H. Drehschmidt. The capillary tube used by Drehschmidt consists of a platinum tube 200 mm. long, 2 mm. external diameter, and 0.7 mm. internal diameter. To both ends of this tube are soldered large pieces of brass tubing. To avoid explosions, the internal space of the capillary is filled throughout its entire length with three or four fine platinum wires.

Clemens Winkler has markedly improved this combustion capillary by providing both ends of it with small water coolers, and in this way has reduced its length to 100 mm.

The arrangement which the author uses in his laboratory is shown in Fig. 71. A platinum tube 100 mm. long, and made according to the directions of Drehschmidt and Winkler, lies between the two cooling tubes *a* and *b*. These tubes are of brass, closed at the lower end, and are about 15 mm. wide and 80 mm. long. The platinum tube is soldered to copper tubes about 3½ mm. wide and bent downward

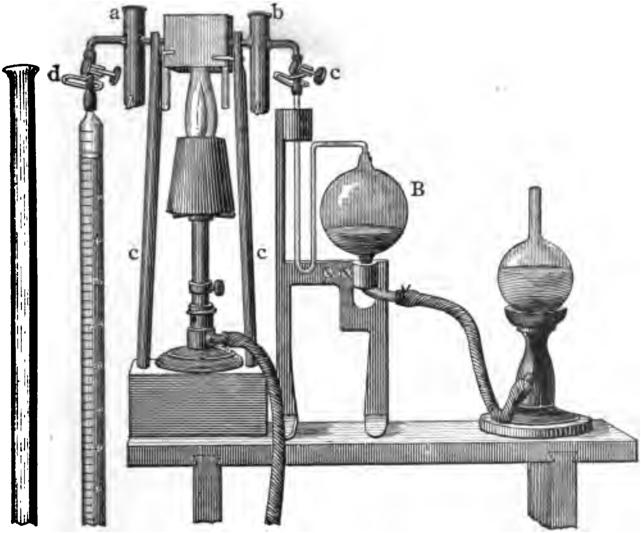

FIG. 71.

at right angles. The contact between the copper and the capillary lies within the cooling tube. The whole apparatus is supported by two iron rods *c* and *c*, which are notched at the top. To keep the heat of the flame away from the cooling tubes as much as possible, a little box of asbestos, open below and provided with an opening in its cover, is placed over the platinum capillary. The propagation of the combustion from the capillary into the combustible mixture in the burette or pipette is made impossible by the insertion of platinum wires into the bent copper tubes. If there are used for this purpose short pieces of platinum wire which fill the interior space of the copper tubes almost completely, a highly explosive gas mixture may be burned without danger of the combustion proceeding from the tubes and causing an explosion in the burette or pipette. When an analysis is being made, the brass cooling tubes *a* and *b* are filled with water. It is not really necessary to fill the platinum tube also with platinum wires for the sake of avoiding an explosion, since the arrangement which has just been described cools the gases so strongly that all gas mixtures are brought below their kindling temperature, but it is nevertheless desirable to fill the platinum tube with platinum wires, so that the internal space of the former may be lessened as much as possible.

To burn a gas with this apparatus, transfer it first to the mercury pipette *B* and close this with the pinchcock. Then measure off in a burette a volume of air or oxygen that is surely sufficient to burn the combustible constituents of the gas mixture. Connect the combustion capillary with the burette and pipette in the manner shown in the figure, and heat the tube to bright redness by means of a flame. Drive the gases back and forth through the capillary by raising and lowering the level-bulb until complete combustion has taken place.

A further advantage of this capillary lies in the fact that it so reduces the temperature of the gases which pass through it that the combustion temperature of nitrogen cannot be reached.

The platinum capillary is undoubtedly the simplest form of combustion apparatus for technical purposes. Perfectly reliable results are given by all three methods — that is, the combustion in the platinum capillary, the explosion with air, and combustion in the combustion pipette with oxygen. The accuracy of the results is in all cases increased if the analyses are made with apparatus that is filled with mercury, and that permits of correction for variations in temperature and pressure.

CHAPTER IV

PARTICULARS CONCERNING THE DETERMINATIONS OF THE VARIOUS GASES

To obtain accurate analytical results, it is of the greatest importance to know exactly the absorbing power possessed by the reagents when manipulated in the pipettes in the manner already described. For this reason the author has determined this absorbing power, his idea here being that it is not so important to know how much of a gas an absorbent may be able to take up under the most favourable circumstances, but rather to ascertain how much it can absorb with a certain rapidity, so that, in spite of the short duration of the absorption in the pipettes, the completeness of this absorption is guaranteed.

For this purpose a pipette with a very fine capillary tube (Fig. 47) was filled with mercury and 1 ccm. of the reagent. The accurately measured reagent is here confined between two columns of mercury, and is thus completely protected from the air. The pipette was then connected, by means of a piece of rubber tubing and a capillary tube, with a simple gas burette containing the gas under consideration. This gas was next drawn into the pipette and shaken as long as a rapid absorption took place, several cubic centimeters at the least disappearing in the space of one minute. Since the figures thus experimentally determined give to the reagent an absorbing power much higher than that which could be relied upon in an analysis, they are divided by four, under the presumption that only a fourth of the reagent should be used if there is to be no doubt as to its absorbing power.

Accordingly, 1 ccm. of approximately 33⅓ per cent caustic potash solution can absorb not merely 40 ccm. of carbon dioxide, as is stated later, but really 160 ccm. The figures thus obtained will be designated as the "analytical absorbing power"; they refer to 1 ccm. of the reagent.

If an accurate account is kept of how much gas the pipette has absorbed, the effectiveness of the reagent remaining in the pipette is always known, and full use of the absorbent can be made without bringing the accuracy of the analysis in question.

OXYGEN

Specific gravity, 1.10521[1]; weight of 1 liter, 1.43003; critical temperature, −118°; critical pressure, 50 atmospheres. Boiling-point under one atmosphere pressure, −181.4°; specific gravity of liquid oxygen $s = 1.124$.

Oxygen is but slightly soluble in water. One liter of water absorbs, from atmospheric air, according to L. W. Winkler,[2] Otto Pettersson, and K. Sonden[3] at 760 mm. pressure: —

---

[1] Most of these figures are from Landolt and Börnstein's *Physikalisch-chemische Tabellen.* The liter weights are referred to Berlin.

[2] *Berichte der deutschen chemischen Gesellschaft*, **21**, p. 2843.

[3] *Ibid.*, 1889, p. 1443.

At 0° C.	10.01 ccm.
" 6° C.	8.3 "
" 9.18° C.	7.9 "
" 14.1° C.	7.05 "
" 16.87° C.	6.84 "
" 23.64° C.	5.99 "
" 24.24° C.	5.916 "

and of pure oxygen, according to Bunsen —

At 20° C., 28.38 ccm.

One volume of alcohol absorbs, according to Carius, at all temperatures between 0° and 24°, 0.28397 volume.

Molten metals take up oxygen with avidity. According to Levol,[1] silver in the fluid condition absorbs about ten times its volume of oxygen and gives it up, with foaming, when gold is added; it also gives it up on simply solidifying, the so-called "spitting" of silver. If silver, melted with access of oxygen, be dropped into water, large bubbles of oxygen are given off by each drop. Cobalt and nickel act similarly.

Oxygen is determined either by combustion with an excess of hydrogen or copper, or by absorption.

The combustion may be carried out with any one of the forms of apparatus described on pp. 130 to 143.

In the combustion with hydrogen, $\frac{2}{3}$ of the volume burned consists of hydrogen, and $\frac{1}{3}$ of oxygen. The volume of oxygen present is hence found by dividing by three the decrease in volume resulting from the combustion.

The necessary hydrogen may be made in the apparatus described on pp. 131 and 133.

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase,* **Part I,** p. 83.

To obtain the greatest accuracy, Bunsen uses hydrogen produced by the electrolysis of water, the positive pole consisting of a zinc wire floating in mercury.[1]

If the explosion pipette is to be used for the combustion, pure oxygen may be burned according to Bunsen's procedure by mixing it with from three to ten times its volume of hydrogen. If larger amounts are added, the inflammability is destroyed, or what is more to be feared, is partially obstructed. If the gas is poor in oxygen, it is mixed with twice its amount of hydrogen; and if the mixture is still not inflammable, electrolytic oxyhydrogen gas is added until complete combustibility is established. The gases should always be vigorously shaken in the explosion pipette before the combustion.

To make sure that the combustion has not taken place near the limit of inflammability, the experiment must be repeated with a somewhat larger amount of oxyhydrogen gas.

If the two experiments do not agree, then only that one made with the larger amount of combustible gas is to be regarded as correct. With some experience, however, one can easily tell from the strength of the explosion whether the proportion of combustible to incombustible gas was such that a complete combustion must have taken place.

Morley in his admirable researches upon the composition of water has carried on combustions of hydrogen with oxygen with a high degree of accuracy.

Very accurate determinations of oxygen may be made by combustion with copper. U. G. Kreusler has so improved the apparatus devised by Ph. v. Jolly for the determination of oxygen in the atmosphere that it is now one of the most exact methods known. A so-called copper eudiometer, whose construction is based upon his well-known air thermometer, is used for the determination. The air whose oxygen contents is to be determined is admitted into a bulb which has previously been completely exhausted, and the pressure is read off on a very exact mercury manometer. The oxygen is then absorbed by a copper spiral that is heated to glowing by a strong electric current; the metallic copper is changed to cuprous and cupric oxide. After the apparatus has become perfectly cool, the remaining nitrogen is brought to the initial volume by changing the pressure, and a reading is taken of the pressure now prevailing.[1] When due regard is given to all the necessary precautions, the method is of the greatest exactness; it is, however, very complex and tedious, and for this reason is not well suited to the making of a large number of determinations.

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[1] Bunsen, *Gasometrische Methoden*, 2d ed. p. 80.

When oxygen is mixed with combustible gases it is necessary to determine it by absorption.

With absorbents a very rapid and, with the use of the necessary precautions, a very accurate determination of oxygen may be made. Good absorbents for oxygen are —

1. A strongly alkaline solution of pyrogallol.
2. Chromous chloride.
3. Phosphorus.
4. Metallic copper.

---

[1] U. Kreusler, *Ueber den Sauerstoffgehalt der atmosphärischen Luft. Landwirthschaftliche Jahrbücher*, 1885, p. 305.

1. *Alkaline Pyrogallol*

The alkaline solution of pyrogallol is prepared by mixing together, either directly in the absorption pipette or in the apparatus to be described later, 5 gr. of pyrogallol dissolved in 15 ccm. of water, and 120 g. of potassium hydroxide dissolved in 80 ccm. of water.

Especial attention must be called to the fact that caustic potash purified with alcohol should not be used, since this preparation, even after quite strong ignition, may cause erroneous results in the analysis.

The absorptions should not be carried on at a temperature under 15°, for it has been observed that the alkaline pyrogallol used for absorption is very much less active at a temperature under 7°. At a temperature of 15° or higher, the last trace of oxygen can be removed with certainty in the space of three minutes by shaking with the solution of alkaline pyrogallol, while at lower temperatures the absorption was not complete after six minutes; moreover, the liquid began to foam, and this, in exact determinations, is very troublesome.

A solution prepared as above gave off no carbon monoxide during the absorption, or at the most only such slight traces that the error thus caused came within the limit of error of the readings.

To ascertain how great the error is which can be caused by the evolution of carbon monoxide, the author's assistant, Herr Oettel, in Dresden, and Herren Kreusler and Tacke, in Bonn, analysed samples of air which were collected by Kreusler in Bonn, and sent to Dresden in bulbs sealed by fusion.

The results were as follows: —

	Analysed by Oettel with Alkaline Pyrogallol	Analysed by Tacke by Combustion with Hydrogen	Analysed by Kreusler with Copper Eudiometer
Sample of May 4, 1886.	20.93 per cent oxygen	20.933 per cent oxygen	20.904 per cent oxygen + carbon dioxide
	20.93 “ “	20.901 “ “	20.931 “ “ + “
Mean:	20.93 per cent oxygen	20.917 per cent oxygen	20.913 “ “ + “
			20.916 per cent oxygen
Sample of May 10, 1886.	20.92 per cent oxygen	20.899 per cent oxygen	20.933 per cent oxygen + carbon dioxide
	20.93 “ “	20.865 “ “	20.919 “ “ + “
Mean:	20.925 per cent oxygen	20.882 per cent oxygen	20.923 “ “ + “
			20.925 per cent oxygen
Sample of May 12, 1886.	20.92 per cent oxygen	20.935 per cent oxygen	20.928 per cent oxygen + carbon dioxide
	20.92 “ “	20.919 “ “	20.914 “ “ + “
Mean:	20.92 per cent oxygen	20.927 per cent oxygen	20.935 “ “ + “
			20.926 per cent oxygen

These results show that determinations made with the copper eudiometer differ from one another by two to three hundredths of a per cent; the same is also true of the analyses made with the hydrogen eudiometer. The pyrogallol method is the most rapid and gives the best agreeing results, so that it appears to be especially suited for parallel analyses.

In technical analysis this solution is used in the double pipette (Fig. 33); in exact analysis in an ordinary pipette (Fig. 47). To effect the absorption, the gas is shaken for three minutes with the solution. The absorption proceeds somewhat slowly and for this reason the pipette shown in Fig. 34 cannot be used. To obtain accurate results a shaking of three minutes is absolutely necessary. The analytical absorbing power of the solution is from 2 to $2\frac{1}{4}$.

If a large number of oxygen determinations are to be made by the "exact" method, the reagent is kept in the apparatus shown in Fig. 72. With this apparatus a large quantity of the reagent may be kept, measured off, and transferred to the absorption pipettes without ever coming in contact with the air.

The large reservoir bulb A ends above in the U-shaped tube B, which has a short side-arm at f and ends in the ⊢-shaped capillary g. To the lower side of the bulb is attached the bent tube h, which is provided with a glass stopcock i. A small funnel can be fastened to the upper end of h by a rubber tube k. A thin rubber tube connects the side-arm f with the funnel o. The ends of the ⊢ capillary g are provided with short pieces of rubber tubing and with pinchcocks. The apparatus is first filled completely with mercury. A funnel or glass tube is then inserted in the free end of *m*, the pinchcocks *n* and *y* are closed, the stopcock *i* is opened, and the aqueous solution of pyrogallol is poured into the funnel attached to *m*. The end *k* of the tube *h* is now connected by a rubber tube with a suction flask, and the flask is joined to an aspirator. Upon opening the pinchcock at *m* the mercury flows through *h* into the flask, and the solution of pyrogallol is drawn into *A*. The entrance of the reagent can be instantly stopped by turning the stopcock *i*. When all of the pyrogallol has entered the pipette, the solution of potassium hydroxide is poured into the funnel and drawn in in the same manner. The two solutions in the apparatus are then thoroughly mixed by shaking.

To transfer some of the reagent to a pipette, the apparatus is arranged as shown in Fig. 72. The capillary of the pipette is inserted at *y* into the end of the rubber tube attached to the lower end of *g*. By blowing into *l* (this can be best done with the rubber pump, Fig. 17) the mercury in the pipette is driven to *g*, and *m*, *n*, and *y* are then closed. Some mercury is poured into the funnel inserted in *k*, and *i* is opened. Upon lowering the funnel *o* and opening the pinchcock *n*, the left side of the U-shaped tube *B* can easily be filled down to a mark with the reagent, for the mercury drives the reagent out of the bulb into *B*. When the reagent has been thus measured off, *i* is closed, *y* is opened, and by raising the funnel *o* the reagent is driven over into the pipette until the mercury reaches the point *x*. The pipette is then disconnected, the capillary *d* is immersed in a beaker of distilled water, and by careful alternate sucking and blowing at *l* the capillary is freed within and without from the last traces of the reagent. It is then dried with filter paper, and the pipette is ready for use.

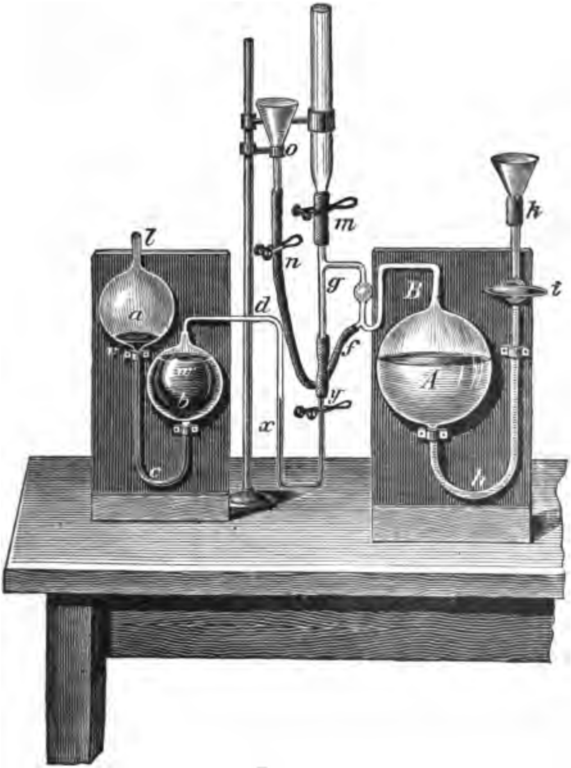

FIG. 72.

2. *Chromous Chloride*

Chromous chloride also may be used for absorbing oxygen.[1] The fact that this reaction is not influenced by hydrogen sulphide or carbon dioxide is further a great advantage. These two gases are completely indifferent to both the blue chromic chloride and the green chromous chloride solutions.

Chromous chloride is the only absorbent that will absorb the oxygen alone in a mixture of oxygen and hydrogen sulphide.

To prepare chromous chloride, Von der Pfordten has used the method given by Moissan. A green solution of chromic chloride free from chlorine is made by heating chromic acid with concentrated hydrochloric acid, and this solution is then reduced with zinc and hydrochloric acid. Since spongy particles always separate from the zinc used for the reduction, the solution must be filtered. For this purpose the reduction is carried on in a flask fitted with a long and a short tube, as is a wash-bottle. The longer tube is bent downward above the flask and is here supplied with a small bulb-tube, which is filled with glass-wool or asbestos. The hydrogen given off during the reduction is allowed to pass out through the longer tube for some time; then after closing its outer end the tube is pushed down into the solution. The hydrogen is thus obliged to pass out through the shorter tube, which carries a rubber valve. Carbon dioxide is then passed into the flask through the short tube, and the chromous chloride solution is driven over into a beaker containing a saturated solution of sodium acetate; a red precipitate of chromium acetate is formed which is washed by decantation with water containing carbonic acid. The red chromium acetate is, relatively speaking, quite unchangeable, and in moist condition it may be kept for an unlimited time in closed bottles filled with carbon dioxide.

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[1] Otto von der Pfordten, Liebig's *Annalen*, **228**, 112.

In washing the red precipitate, some free acetic acid is added in the beginning, to dissolve any basic zinc carbonate which may have been thrown down. In this way a preparation completely free from zinc is obtained.

To absorb oxygen, the chromium acetate is decomposed by the addition of hydrochloric acid, the air being excluded. It is advisable to use an excess of chromium acetate in order to avoid the presence of free hydrochloric acid.

3. *Phosphorus*

The absorption of oxygen with phosphorus, as described by Lindemann, is much more convenient than the two preceding methods. To obtain the phosphorus in the necessary stick form, it is melted under water in a test-tube placed in a water bath, the temperature of the water being about 50°. Enough phosphorus is used to form a column about 6 cm. high. A slightly conical glass tube of 2 to 3 mm. internal diameter is then dipped into the molten phosphorus, the upper end of the tube is closed with the finger, and the tube is lifted out and dipped immediately into a tall beaker full of water. A peculiar movement takes place in the phosphorus enclosed in the tube at the moment when it solidifies, and since the phosphorus undergoes a marked decrease of volume when it becomes solid, the stick usually falls out of the tube upon gentle tapping; if it adheres, it can easily be pushed out with a wire.

These phosphorus sticks are used in the absorption pipette for solid and liquid reagents (Fig. 32); the cylindrical part is filled as full as possible with the sticks, the remaining space being filled with distilled water.

To make the absorption, the gas whose oxygen contents is to be determined is driven over into the pipette, thereby displacing the water and coming into contact with the moist sticks of phosphorus. A bright glow is visible when the reaction proceeds normally; the phosphorus burns to phosphoric acid, phosphorus acid, etc., at the expense of the oxygen. After three minutes, at the longest, the absorption is complete. The end of the absorption is sharply shown by the disappearance of the glow when the pipette is in a dark room.

Since the different oxidation products of phosphorus are all soluble in water, the surface of the sticks of phosphorus is kept fresh by the action of the confining water alone, if that be renewed from time to time. And further, since these oxidation products, as solid and liquid substances, have a very small tension, no error is caused by the white cloud which may be present in the gas residue after the absorption. The phosphorus can of course be used for a very large number of analyses, if it is protected from the action of the light. To do this the cylindrical part of the pipette is covered with a small box, or the whole pipette is covered, when not in use, by a light-tight box of wood or cardboard.

Parallel analyses showed that the absorption with phosphorus is very complete, and hence this Lindemann process for the determination of oxygen must be classed among the finest of gas analytic methods, it being of especial value because with one filling of the pipette enormous quantities of oxygen may be absorbed, while alkaline pyrogallol possesses a relatively small absorbing power.

Naturally the method cannot be used under those conditions in which phosphorus is no longer able to unite with oxygen. Detailed experiments have been made upon this point by Schönbein in his researches upon ozone. He states that the reaction is entirely or partly prevented by the presence of ethylene ($\frac{1}{400}$ volume of ethylene is sufficient) and other hydrocarbons or ethereal oils, alcohol, and traces of ammonia.

Moreover, oxygen does not act upon phosphorus when the gas has a very large partial pressure. If phosphorus be brought into contact with oxygen of the density of the atmosphere, no reaction whatever takes place, and not the least light is seen. If, however, the oxygen be diluted with another gas, or mechanically by the air-pump, the reaction begins when the gas has been brought to about 75 per cent of its initial partial pressure. At first a feeble glow is seen and then suddenly, with a sort of explosive flash of light, the oxygen *burns*, the phosphorus being partly melted.

The reaction takes place normally in gases which do not contain more than 50 per cent of oxygen.

To investigate gases which are rich in oxygen, it is advisable to dilute them with an equal volume of nitrogen made from air by absorbing the oxygen with phosphorus. Mixtures of oxyhydrogen gas and air even when highly diluted may become so strongly heated as to cause an explosion.

The reaction is further dependent upon the temperature.

It proceeds normally at about 20° C., while at 14° it takes place quite slowly, so that a quarter of an hour or longer is required to completely separate the oxygen from 100 ccm. of air. At 10° and still lower temperatures a half hour's time would not be sufficient. It follows from this that during the colder months of the year the absorption must be carried out in warmed rooms.

4. *Copper*

Copper at a red heat or at ordinary temperatures may be used for the absorption of oxygen.

The method of Jolly, in which a copper wire is electrically heated to glowing, has been mentioned above. Copper powder made by reducing granular copper oxide with hydrogen may also be employed. If a hard glass tube, filled with this powder, be heated to red heat in a combustion furnace and the gases be then led through the tube, they can in this manner be completely freed from oxygen.

A very active absorbent for oxygen is metallic copper in the form of little rolls of wire-gauze, immersed in a solution of ammonia and ammonium carbonate.

It has long been known that many metals oxidise readily in the presence of vapour of ammonia. The absorption of oxygen, however, takes place rapidly only so long as the metallic surface is bright, and it proceeds very slowly as soon as considerable quantities of oxide are formed.

By the admirable researches which C. Schnabel has made upon the solubility of the oxides of zinc, copper, etc., in ammonium carbonate, in connection with his work upon the desilverisation of lead by zinc,[1] the author was led to make experiments to see whether it might not be possible to effect a complete absorption by using ammonium carbonate as a solvent for the oxides formed. Experiments showed that oxygen is completely and quickly absorbed when brought into contact with copper and a solution of commercial ammonium carbonate, but that at the same time not inconsiderable quantities of carbon dioxide are given off. When zinc was used, a simultaneous evolution of hydrogen took place, and iron proved to be very slow in its action, as was to be expected from the insolubility of its oxide. Further experiment showed that a very rapid and complete absorption of oxygen results, without any other gas being at the same time given off, when the oxygen is brought into contact with metallic copper and a solution consisting of equal parts of a saturated solution of pieces of commercial ammonium sesquicarbonate, and a solution of ammonia of 0.93 specific gravity. Such an ammoniacal solution has a tension which may in most cases be disregarded, and, provided that the absorption apparatus contains sufficient metallic copper, the solution can easily absorb 24 times its volume of oxygen. Hence its analytical absorbing power is 6. Since the surface of metallic copper is frequently covered with a thin layer of grease, it is necessary to clean it before using by exposing it for a moment to the action of nitric acid.

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[1] *Zeitschrift für das Berg-, Hütten- und Salinenwesen im preussischen Staate*, 28.

The reagent is used in the same manner as phosphorus, in a pipette for solid absorbents. In making the absorption, the gas is allowed to remain in the pipette for five minutes.

The method described admits of a very rapid and exact determination of oxygen, and is to be preferred to the ordinary methods with alkaline pyrogallol and phosphorus, provided that the gases do not contain carbon monoxide. As compared with alkaline pyrogallol, copper has a much greater absorbing power for oxygen, and it has the advantage over phosphorus, aside from the danger attending the use of the latter, of absorbing equally well at any temperature, while the absorption of oxygen by phosphorus takes place very slowly at temperatures below 14° C. Direct experiments showed that, at a temperature of −7° C., the absorption of oxygen in the air was complete in five minutes.

In the analysis of gas mixtures which contain carbon monoxide the method cannot be used, because the basic ammonium cuprous carbonate, formed from the copper present, absorbs carbon monoxide.

The oxygen in gas mixtures containing carbon monoxide can, according to Kostin, be removed by the use of a pipette filled with iron wire gauze that stands in a saturated solution of ferrous sulphate to which has been added one-third of its volume of strong ammonia. The author has found that it is still better to employ a solution of ferrous chloride to which has been added ammonia and sufficient ammonium chloride to prevent the separation of ferrous hydroxide.

OZONE

A large number of reagents may be used for the detection of ozone. For the detection of such small amounts of ozone as are present in the atmosphere, so-called ozone papers are employed.

Houzeau has suggested that this be prepared by dipping strips of Swedish filter paper into a wine-red litmus solution which contains in a cubic centimeter about 0.013 g. of the extracted constituents dried at 100°; the paper is dried and then impregnated to a fourth of its length with a one per cent solution of neutral and pure potassium iodide free from iodate. The dried paper must be protected from the air, and is on this account kept in tightly closed bottles.

This paper is coloured slightly blue by from 0.0002 to 0.0003 mg. of ozone. In air containing $\frac{1}{261000}$ of its weight of ozone, the paper turns blue at once. The part of the paper which is coloured with the litmus solution and is not impregnated with the potassium iodide, serves to show the presence in the air of acid or alkaline substances which might influence the reaction. By the action of ozone the potassium iodide is decomposed and potassium hydroxide is formed, which turns the litmus paper blue. Chlorine, nitric acid, and other acid substances do not of course turn the paper blue: in this respect it is superior to those which follow.

According to Schönbein, strips of paper are saturated with a dilute starch and potassium iodide solution (1 KI + 10 starch + 200 water), and these strips are exposed to the air. A distinction of ten shades from white to dark blue is made.

Wurster[1] uses tetra-methyl-para-phenylene-diamene, which, upon taking up one atom of oxygen, is quantitatively oxidised to a blue colouring matter, and by further union with six oxygen atoms changes to a colourless substance. At Wurster's suggestion, Dr. Schuchardt in Görlitz has made a colour scale containing eight numbers. These are obtained by the action of one or two drops of standard iodine solutions upon the tetra-paper : —

The normal iodine solutions	$\frac{1}{250}$	$\frac{1}{500}$	$\frac{1}{1000}$	$\frac{1}{2500}$	$\frac{1}{5000}$	$\frac{1}{10000}$	$\frac{1}{33000}$	$\frac{1}{100000}$
correspond to the numbers on the colour scale	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
And hence contain milligrams of active oxygen in the liter	32	16	8	3.2	1.6	0.8	0.24	0.08

Or if 16,000 drops are reckoned to the liter : —

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Milligrams active oxygen in a drop	0.002	0.001	0.0005	0.0002	0.00001	0.000005	0.0000015	0.0000005

A blue coloration of any one of the three papers may be caused either by ozone or by hydrogen peroxide.

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1888, p. 921.

According to G. Erlwein and Th. Weyl[1] ozone imparts to a hydrochloric acid solution of m-phenylendiamin a Burgundy-red colour, while both hydrogen peroxide and nitrous acid are without action.

Engler and Wild[2] state that ozone may be detected with manganous chloride paper which is moistened with guaiacum tincture. If ozone is present, a blue colour appears, but the paper is not affected by either hydrogen peroxide or nitrous acid. Ammonium carbonate imparts a brown colour to the manganous chloride paper, but not a blue. Free halogens and hypochlorites must, however, be excluded.

On account of the greater delicacy of potassium iodide starch paper it is better to detect ozone in the presence of hydrogen peroxide by first removing the latter by passing the gases through a tube filled with glass beads and solid chromic acid and then introducing into the gas a piece of potassium iodide starch paper. Hydrogen peroxide is completely removed by both dilute and concentrated solutions of chromic acid, but ozone is not acted upon by this reagent. Attention is also called to the fact that the reactions of hydrogen peroxide upon chromic acid and ether, and upon titanic acid, are not very delicate.

A very delicate reagent for hydrogen peroxide is a solution containing potassium ferricyanide and ferric chloride. The mixture has at first a brownish or greenish colour, but small amounts of hydrogen peroxide change it to blue.

To detect ozone, the paper prepared by one of the foregoing methods is fastened over the end of a glass tube by means of a rubber band, and a measured quantity of gas is drawn through the tube by an aspirator.

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1898, p. 3158.
[2] *Ibid.*, 1896, p. 1940.

To determine larger amounts of ozone it is best to lead the gas through a solution of potassium iodide and to then acidify the solution and titrate the iodine set free with a solution of sodium thiosulphate.[1]

The reaction is the following: —

$$O_3 + 2\,KI + H_2O \doteq O_2 + 2\,KOH + I_2.$$

As absorbent either cinnamon oil or turpentine oil may be employed; these take up the ozone completely, and are able to absorb very large amounts of the gas.

Especial attention should be called to the fact that rubber is very strongly attacked by ozone. When the gas is to be led some distance, the bell connection (Fig. 73) devised by Engler and Nasse is well adapted for making the connections. *a* is a bent glass tube over whose end a wide glass tube is fitted by means of a cork *c*. The little cup thus formed is filled with mercury, into which dips the bell *b*.

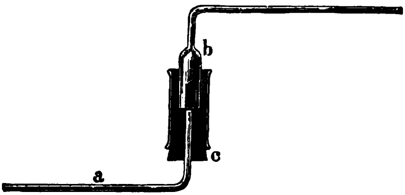

FIG. 73.

NITROGEN

Specific gravity, 0.97010. Weight of 1 liter, 1.2505. Nitrogen is but slightly soluble in water, one volume of water absorbing, according to Bunsen, at 760 mm. pressure and $t°$,

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[1] The investigations of Ladenburg and Quasig, *Berichte der deutschen chemischen Gesellschaft*, 1891, p. 1184, have shown that if the solution is not acidified, erroneous results are obtained.

$$0.020346 - 0.00053887\,t + 0.000011156\,t^2 \text{ vol. of nitrogen:}$$

hence at

5°, 0.01794 vol.
10°, 0.01607 "
15°, 0.01478 "
20°, 0.01403 "

Otto Pettersson and K. Sonden[1] state that at a pressure of 760 mm. 1 liter of water absorbs from the air:—

At 0°, 19.53 vol.
" 6°, 16.34 "
" 9.18°, 15.58 "
" 14.10°, 14.16 "

According to Carius, one volume alcohol takes up at $t°$,

$$0.126338 - 0.000418\,t + 0.000006\,t^2 \text{ vol. of nitrogen;}$$

hence at

20°, 0.122378 vol.

Critical temperature, −146°; critical pressure, 35 atmospheres; boiling-point, −194.4°; specific gravity of liquid nitrogen, at −194.4° = 0.885; melting-point, −214°.

The residue in gas mixtures which cannot be determined either by the ordinary absorption methods or by combustion was earlier considered to be nitrogen alone. Consequently all of the errors in the preceding determinations were concentrated upon the value found for nitrogen, and the results for this element were the more inexact as the gas mixture increased in complexity. The investigations of W. Ramsay and Lord Rayleigh have shown that with this nitrogen the gases of the argon group may be present. In order to separate nitrogen from these gases, we may employ as absorption agent glowing magnesium, lithium, or barium carbide, or, following the procedure of Cavendish, the nitrogen may be caused to unite with oxygen by means of a strong electric spark. Erdmann states that the combustion is appreciably aided by the presence of water vapour and ammonia.

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1889, p. 1443.

Maquenne has recommended for the absorption a mixture of magnesium with lime that has been strongly ignited in hydrogen.

In order to be able to judge of the efficiency of these various absorption agents, the author placed the different substances in hard-glass tubes, exhausted these tubes of air, and then introduced an excess of nitrogen. The tubes were then heated to bright redness, the nitrogen was pumped out and measured, and the amount of that gas which has been held back by each absorbent was thus determined.

The results were as follows: —

Absorption Agent Employed	Number of Cubic Centimeters of Nitrogen which was absorbed in Fifteen Minutes	Number of Cubic Centimeters of Nitrogen which was absorbed in One Hour
1 gram magnesium powder, medium fine	——	14.5
1 gram lithium	——	73.5
1 gram magnesium and 5 grams quicklime. The lime was not freshly ignited. . . .	94.5	112.0
1 gram magnesium and 3 grams quicklime. The lime was not freshly ignited. . . .	——	50.0
1 gram magnesium and 8 grams quicklime. The lime was not freshly ignited. . . .	——	31.4
1 gram magnesium and 5 grams quicklime. The lime was highly ignited shortly before the experiment	86.4	122.5
1 gram magnesium, 5 grams freshly ignited lime, and 0.1 gram metallic sodium . . .	201.0	287.0
1 gram magnesium, 5 grams freshly ignited lime, and 0.25 grams metallic sodium . .	196.0	326.2
1 gram magnesium, 5 grams freshly ignited lime, and 0.11 grams metallic mithium . .	169.0	228.0

Ignited lime with metallic sodium alone absorbed no nitrogen whatever, and only very slight absorption is effected by barium carbide alone, barium carbide and potassium, barium fluoride and sodium, or amorphous boron and silicon. It is possible that the barium carbide used in these experiments decomposed partially when it was pulverised.

From these experiments the author considers that the best absorption agent for nitrogen is a mixture of one part by weight of finely powdered magnesium with five parts by weight of freshly ignited lime in pieces about as large as poppy seeds and 0.25 part by weight of metallic sodium. The magnesium should be intimately mixed with the ignited lime, but it is sufficient to add the sodium in the form of a number of pieces each about half as large as a pea. The layer of oxide covering the metallic sodium should be first removed, and the metal should be added to the mixture just before using.

The "analytical absorbing power" of the mixture, based upon the amount of the magnesium, is 8.15 ccm.

GASES OF THE ARGON GROUP

	Density	Melting-point	Boiling-point at 760 mm.	Critical Temperature	Critical Pressure mm.	Weight of 1 ccm. of the Liquified Gas at its Boiling-point	Specific Gravity	Weight of 1 liter
Helium .	1.98						0.14	0.18
Neon . .	9.96							
Argon .	19.96	−187.9	−186.1	−117.4°	40.2	1.212	1.352	1.788
Krypton,	40.78	−169.	−151.67	− 62.5°	41.24	2.155		
Xenon .	64.	−140.	−109.1	+ 14.75°	43.5	3.52		

Since the gases are monatomic, their atomic weights are twice their specific gravities as referred to hydrogen.

Helium cannot be condensed even at a temperature of −264°. 100 ccm. of water at 18° absorbs 0.7 ccm. of the gas.

One liter of water at room temperature dissolves 40 ccm. of gas.

Neon and helium may be separated by means of the different solubilities and liquid oxygen.

After the absorption of nitrogen the gases of the argon group remain behind. Their separation may be effected by cooling the gases down to extremely low temperatures by means of liquid air, and then allowing them to fractionally distil. The purity of the gases may be judged from the specific gravity.

The gases may be recognized from their spectra, which may be obtained by bringing the gases into Plücker tubes, and using an induction coil of from 4 to 7 mm. spark length, and furnishing about 20 sparks per second.

Argon and xenon exhibit very noticeable changes in the positions of the spectrum line when a Leyden jar is introduced into the circuit, but this does not cause a change in the spectra of the other gases of the argon group.

Helium is chiefly characterised by a very bright yellow line, which is very close to the sodium lines, but lies slightly nearer the violet end of the spectrum than do the latter.

Neon shows red, orange, and yellow lines, while krypton yields a brilliant green line.

The argon spectrum varies greatly with the pressure and the strength of the discharge, and shows a large number of lines in the red, green, and violet parts of the spectrum. The spectrum lines of neon, krypton and xenon cannot be seen in the spectrum of impure argon. Even photographs of the spectra fail to disclose them.

Xenon shows a very brilliant line in the blue.

Further details may be found in the published articles of Rayleigh, Ramsay, and Crookes, and coloured charts of the spectra are given in the second edition of Erdmann's *Lehrbuch der anorganischen Chemie.*

Tubes filled with argon may be easily prepared by extracting the gas from atmospheric air. Helium can be obtained by heating pulverised cleveite with twice its weight of primary potassium sulphate, using the apparatus shown in Fig. 12.

For the separation of the gases of the argon group the author would recommend the apparatus shown in Fig. 74. *B* is a tube of hard glass which is filled with a mixture of one part by weight of metallic magnesium, 0.2 parts of metallic sodium, and five parts by weight of freshly ignited lime that has been broken into pieces about as large as poppy seeds. The tube *A* permits of the easy introduction of the gases to be examined. The spaces *D*, *E*, and *F* are filled with coarse-grained copper oxide, potassium hydroxide, and phosphorus pentoxide respectively, and to these is attached an air-pump, not shown in the figure, by means of which the gases can be removed and collected. (The Töpler air-pump, described on p. 393, may be used for this purpose.) The tubes are connected by means of U-shaped thin glass tubes, which are joined by pieces of rubber tubing. These joints are made completely air-tight by immersing them in mercury which is

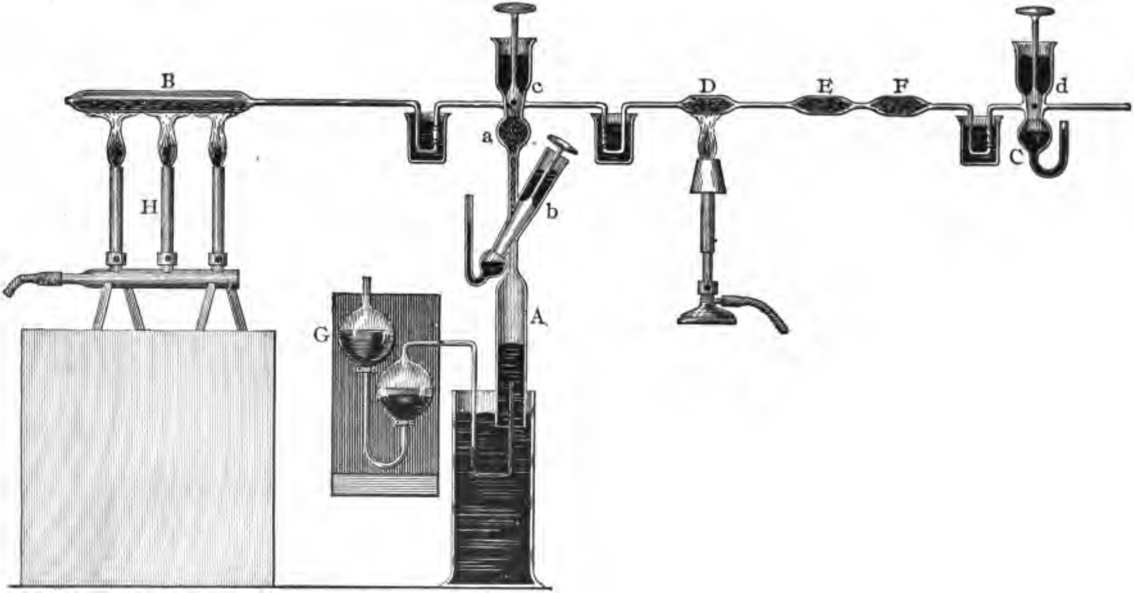
B
c
D
E
F
d
a
C
H
b
A
G

FIG. 74.

placed in small beakers. This arrangement makes it easy to connect and take apart the different parts of the apparatus, and gives it sufficient freedom of motion to render it but slightly liable to breakage. By means of the two-way stopcock *c* the tubes *A* and *B* may be brought into communication with each other, or either one of them may be joined to the air-pump. This stopcock should be very carefully ground. Lanoline has been found to be a satisfactory lubricant for the stopcocks.

The stopcocks *b* and *d* are also provided with mercury cups to insure the tightness of the joint.

The bulb *a* is filled with phosphorus pentoxide. Loose wads of asbestos are placed in all of the tubes which contain absorbing agents so as to prevent particles of these substances from being carried along through the tubes.

In making an analysis, all the tubes are first nearly exhausted of air with an air-pump, and mercury is drawn up in the tube *A* until it reaches the stopcock *b*. The tube *B* is then slightly heated by means of a row of Bunsen burners. This causes an evolution of a considerable amount of gas from the mixture contained in the tube. When the tube is again nearly free from air, the tube *D* is then heated and the exhaustion is continued with the air-pump until the amount of gas removed with each stroke of the pump is so small as to be negligible. This operation takes about two hours. If the pressure in the apparatus is to be reduced to a very low point, it is absolutely necessary that the air-pump should be perfectly dry on the inside and that the mercury should be free from particles of dust. Like many other liquids, mercury possesses the property of holding dust in suspension, and this dust will not completely separate even after days of standing. If the mercury air-pump and the mercury are not thoroughly clean, the pumping may be continued for hours without producing high dilution of the gas in the apparatus, but the exhaustion is accomplished in a very short time if the apparatus is clean and perfectly dry.

When the apparatus has thus been made ready, the gas to be examined is introduced into *A* from the gas pipette *G*. It is necessary to previously free this gas mixture from all absorbable and combustible constituents. The stopcock *c* is closed, and the gas is allowed to enter the bulb *a* by slowly opening the stopcock *b*. *a* is filled with phosphorus pentoxide, *b* is then closed, and *c* is turned into such position that the tube *B* communicates with the bulb *a*. Upon carefully opening *b* mercury rises in *A* and drives before it any gas therein contained, but the greatest care must be exercised to prevent any mercury whatever from entering the bulb *a*. If only a very small volume of gas is at one's disposal, it can be swept up into the apparatus by means of pure hydrogen gas, which is introduced into *A* from a gas pipette. After about a quarter of an hour the stopcock *d* is closed and the residual gases of the argon group may be allowed to enter *D*, *E*, and *F*. Gas is then again drawn out from *a*. The stopcock *d* is necessary to prevent the too rapid flow of the gases through *D*, *E*, and *F*, and the consequent passage of unburned gases through the glowing copper oxide in *D*. If the stopcock *d* were not present, the gas mixture would of course rush with great rapidity through *D*, *E*, and *F* into the exhausted bulb of the mercury air-pump. The necessity for introducing glowing copper oxide, caustic potash, and phosphorus pentoxide into the apparatus arises from the fact that it is impossible to completely remove the last traces of absorbable gases by means of the ordinary absorption methods.

When the whole gas volume under examination has been in the tubes *B*, *D*, *E*, and *F* for some time, the stopcock *d* is carefully opened and the gas residue in the apparatus is drawn over with the mercury air-pump into the graduated tube *E* (see Fig. 115) and is here measured. If the gas volume is very small, it is better to transfer it directly to a measuring bulb and to measure it in the apparatus for exact gas analysis.

If a spectroscopic examination of the gas residue is desired, there is introduced between the stopcock *d* and the mercury air-pump a four-way glass tube. To one arm of this tube is attached a glass tube filled with gold leaf and to this is joined a Plücker tube. To the other three arms of the four-way piece are attached the stopcock *d*, the mercury air-pump, and a manometer tube. The manometer tube is indispensable, because the spectra of the gases vary with the pressure. If this spectroscopic examination is to be made, it is best to first measure the gases and then to transfer them to *A* by means of a pipette and to allow them to again pass through the tube *B*. The tubes *B* and *D* always break upon cooling, so that it is necessary to keep them hot during the whole procedure. The temperature of these two tubes should be raised to the softening point of the glass.

HYDROGEN

Specific gravity, 0.069234; weight of 1 liter, 0.089582; critical temperature, 233°; critical pressure, 15 atmospheres; boiling-point, about −240°; specific gravity (water = 1) of liquid hydrogen, 0.07.

According to L. W. Winkler,[1] one volume of water absorbs at

0°, 0.02148	vol. hydrogen
5°, 0.02044	"
10°, 0.01955	"
15°, 0.01883	"
20°, 0.01819	"

At $t°$ alcohol takes up

$$0.06925 - 0.0001487\,t + 0.000001\,t^2 \text{ vol. of hydrogen;}$$

hence at

20°, 0.066676 vol. (Bunsen).

Hydrogen can be very easily determined by burning it with oxygen. Either air is used, or, as proposed by Bunsen, pure oxygen made in retorts blown from a glass tube, and of from 6 to 10 ccm. capacity (Fig. 75). These retorts are half filled with dried and pulverised potassium chlorate, and the end of the delivery tube is then heated at *a* and bent upward. The air is first driven out by a rapid evolution of oxygen, and the gas is then led directly into the eudiometer, care being taken that the volume

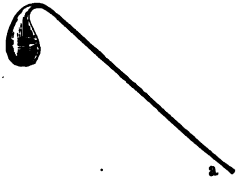

FIG. 75.

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[1] *Berichte der deutschen chemischen Gesellschaft*, **24**, 89. See also Timofejew, *Zeitschr. für phys. Chem.* **6**, 141.

of oxygen does not amount to more than three or four times that of the hydrogen to be determined.

The quantity of hydrogen present is $\frac{2}{3}$ of the volume disappearing in the combustion. If the mixture contains absorbable constituents also, these are first absorbed and the residual gas is then used for the analysis.

When nitrogen is present a considerable error may be caused by not avoiding, in the combustion, the temperature at which nitric acid is formed. Hence one should never neglect to calculate, after the experiment, the proportion of nitrogen to the oxyhydrogen gas burned. If this was less than 6 to 1, the analysis must be repeated with the addition of so much air that this proportion or a still greater amount of nitrogen will be present.

If, on the other hand, the proportion of hydrogen to incombustible gas be very small, such an amount of electrolytic oxyhydrogen gas is added that complete combustion will result. The oxyhydrogen gas disappears completely in the combustion, and hence need not be exactly measured.

An accurately measured amount of pure hydrogen mixed with an excess of air may be used instead of the oxyhydrogen gas. The contraction resulting from the hydrogen added must then be allowed for.

The combustion is made either in the explosion pipette by ignition with an electric spark, or in a glass tube filled with palladium-black, or, as Winkler has proposed, with palladium asbestos. The advantage of the combustion with palladium is, that in a mixture of hydrogen, marsh-gas, and nitrogen, the hydrogen alone may be burned: this is known as fractional combustion.

Hydrogen may also be very accurately determined by means of the method proposed by Dennis and Hopkins[1] with the combustion pipette described on p. 138 and the arrangement of apparatus shown on p. 294. In this method the hydrogen is first introduced into the combustion pipette and a mixture of equal parts of oxygen and air more than sufficient for its combustion is measured off into the burette. The burette and pipette are then connected, the spiral is heated to redness by means of an electric current, and the mixture of air and oxygen is slowly passed over from the burette into the pipette. The combustion of the hydrogen is complete almost as soon as sufficient oxygen has been introduced. When the combustion is finished, the residual gas is passed back into the burette and measured. The results of a series of determinations of hydrogen made with this method are given in the following table: —

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	ccm.	ccm.	ccm.	ccm.	ccm.	ccm.	ccm.	ccm.
Hydrogen taken	99.6	100.0	98.6	99.8	99.4	95.35	97.5	51.15
Oxygen and air added	99.6	99.95	99.9	100.0	99.1	96.6	99.75	48.95
Total . . .	199.2	199.95	198.5	199.8	198.5	191.95	197.25	100.10
Residue after combustion . .	50.0	50.1	50.8	50.55	49.7	49.1	51.2	23.4
Contraction . . .	149.2	149.85	147.7	149.25	148.8	142.85	146.05	76.7
Equivalent to hydrogen . . .	99.47	99.9	98.47	99.5	99.3	95.23	97.37	51.13
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
Hydrogen found	**99.9**	**99.9**	**99.9**	**99.7**	**99.9**	**99.9**	**99.9**	**100.0**

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[1] *J. Am. Chem. Soc.*, **21**, 398.

FRACTIONAL COMBUSTION

The possibility of separating gases from one another by fractional combustion was first observed by W. Henry, and used by him for the analysis of gas mixtures.

Henry states[1] that carbon monoxide and hydrogen can be removed by combustion from a mixture of hydrogen, carbon monoxide, marsh-gas, and nitrogen by leading these gases over platinum sponge heated to 177°.

Since no convenient method for carrying out this reaction was devised, it had not been adopted into gas analysis.

While studying the occlusion of hydrogen by palladium, the author succeeded in working out a method[2] by which the hydrogen in a mixture with marsh-gas and nitrogen may be fractionally burned in a very short time at the temperature of the room.

The following points concerning the fractional combustion were determined: —

1. A mixture of hydrogen with oxygen in excess, led over palladium sponge which has been superficially oxidised by heating it to redness and allowing it to slowly cool, is completely burned. The reaction begins at the temperature of the room, and so much heat is developed that the palladium begins to glow and the gases explode if they are present in the proper proportions to form oxyhydrogen gas.

2. Marsh-gas, mixed with oxygen, and led over palladium, does not burn at temperatures up to 100°;

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[1] *Annals of Philosophy*, **25**, 428.

[2] *Berichte der deutschen chemischen Gesellschaft*, 1879, p. 1006.

the combustion begins at about 200°. A mixture of 29.3 ccm. marsh-gas and 70.6 ccm. oxygen, led several times over palladium heated to from 200° to 220°, underwent a contraction of 3 ccm.

3. Mixtures of hydrogen, marsh-gas, and oxygen, in the proportions necessary for combustion, often explode very violently when brought into contact with palladium; the author did not succeed in preventing the explosion with certainty, even by the interposition of cooling metals and by the use of thin tubes standing in water.

4. If mixtures of hydrogen, marsh-gas, and air, oxygen being present in excess, be led over palladium at ordinary temperatures up to 100°, the hydrogen alone burns, and the marsh-gas is not at all acted upon, provided that the palladium is not allowed to heat up too much during the reaction. No explosion takes place here.

If the water formed in the combustion is driven off from time to time by heating the palladium upon the cover of a platinum crucible, the palladium does not then need to be regenerated after each experiment, but may be used as it is for a large number of combustions. Since the palladium plays only an intermediary *rôle*, a very small amount of it suffices.

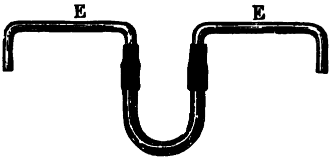

FIG. 76.

In the following researches 0.5 g. of the metal was placed in a U-shaped glass tube (Fig. 76), which by means of two capillary tubes *E* was connected on the one side with a gas burette, and on the other with a gas pipette filled with water. The U-shaped tube was kept cool by immersing it in a beaker glass containing water of the temperature of the room. The gases were led through so slowly that the metal either did not glow at all or was heated to redness at some points for only a very short time. A single passage of the gas mixture through the palladium sufficed usually for complete combustion.

Composition of the Gas Mixture			Resulting Contraction	Hydrogen calculated from the Contraction
Hydrogen	Marsh-gas	Air		
1.5	12.0	85.1	2.3	1.5
3.0	8.3	86.5	4.5	3.0
5.1	12.3	86.0	7.6	5.0
9.3	7.1	83.7	14.1	9.4
13.7	7.3	77.5	20.3	13.5
14.1	5.4	81.2	21.2	14.1
14.6	4.5	80.6	22.1	14.7
13.1	6.0	80.3	19.7	13.1

In the last experiment the palladium tube stood in water at 100°.

From these experiments it follows that, with the addition of air, the hydrogen in any mixture of hydrogen, marsh-gas, and nitrogen may be determined by fractional combustion at about 100°. For mixtures which, like all furnace or generator gases, contain large amounts of nitrogen, pure oxygen also may be employed.

Cl. Winkler has later suggested that, in place of the tube filled with palladium-black, there be used a capillary tube which contains a very small quantity of palladium asbestos, and which is heated from without by a little flame to the temperature of the reaction. If hydrogen alone is to be burned, this arrangement is quite suitable; if, however, a fractional combustion is to be made, the author prefers the arrangement described above, since with direct heating it is difficult to control the temperature. If the temperature rises beyond 200°, a part of the marsh-gas is burned with the hydrogen. If, however, the palladium tube stands in hot water, the temperature easily regulates itself.

Hydrogen may also be determined by absorption with palladium, potassium, or sodium.

ABSORPTION OF HYDROGEN BY PALLADIUM

Many endeavours to find an absorption method for separating hydrogen from other gases led the author to ascertain the conditions under which the property of palladium of condensing large amounts of hydrogen at 100°, known as occlusion, may be used for quantitatively separating hydrogen from marsh-gas and nitrogen, as well as from some other gases.

Concerning the purely chemical relations between hydrogen and palladium, a large number of experiments have shown the author—

1. That, on the one hand, palladium loses, as is well known, its silver-white metallic colour when heated nearly to a red heat in the presence of oxygen,

and becomes superficially covered with a thin layer of palladious oxide, and that this palladious oxide is, on the other hand, able to burn hydrogen at ordinary temperatures with evolution of heat, so that the intermixed or reduced metallic palladium reaches the temperature at which it can absorb large quantities of hydrogen by occlusion.

2. That the hydrogen taken up by occlusion may be completely removed either by heating the palladium in a vacuum to 100°, or by leading air over the metal at ordinary temperatures. This latter was proved by saturating palladium with hydrogen to the fullest extent possible, by placing the metal in a red-hot tube and leading dry hydrogen over it, and then letting it slowly cool in the current of hydrogen. Air having been led over the palladium thus prepared, the metal was placed in a porcelain tube connected with a Töpler air-pump, and the tube was raised to bright red heat, but no further trace of hydrogen could be obtained.

3. That upon leading air over palladium which had occluded large quantities of hydrogen, the temperature of the metal is raised so high by the combustion that palladious oxide is again formed.

A mixture of hydrogen, marsh-gas, and nitrogen is indifferent to pure metallic palladium, but a strong reaction takes place when the gases are brought into contact with palladium sponge which has been covered with a very thin layer of palladious oxide by heating it to glowing and letting it cool not too rapidly. The palladium becomes warm and the hydrogen disappears completely, provided the gas is brought into sufficiently intimate contact with the palladium. If air be led over the palladium after the completion of the reaction, which is clearly indicated by the cooling of the metal, the hydrogen in the metal burns and the surface is again covered with palladious oxide. The palladium thus regenerated with air is at once ready for a new absorption; with a few (2.5) grams of palladium sponge in a glass tube an unlimited number of absorptions may be made without the aid of external heat. The reaction concerned is partly combustion, partly occlusion.

What has just been said holds true only when the gases are mixed in certain proportions, since of course the conditions for the regeneration of the palladium exist only when large amounts of hydrogen have been occluded. The presence of sufficient hydrogen can easily be brought about by the addition of pure hydrogen made in the apparatus already described. (The procedure here is similar to the addition of oxy-hydrogen gas in the explosion analysis.) Yet even when the hydrogen is added, the reaction fails if the gas mixture to be analysed contains certain other substances, as it always does in technical analyses. We have there to deal with very complicated gas mixtures from which the other gases — carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, etc. — must first be separated by absorption. The gases just mentioned may in a few minutes be separated by absorption with great ease and with a completeness more than sufficient for practical ends, so that less than tenths of a per cent of the gases remain in the gas residue. It is, however, very difficult, and, in a short space of time, impossible to separate traces less than tenths per thousand, for the well-known reason that the rapidity of absorption diminishes with the dilution of the gas. And since, further, some of the absorbents give up gases — the solutions of cuprous chloride give off, according to whether they are acid or alkaline, either hydrochloric acid or ammonia — the residue which remains after the absorption of the absorbable gases consists of hydrogen, nitrogen, and marsh-gas, and an undeterminable amount of carbon dioxide, heavy hydrocarbons, oxygen, and vapours of hydrochloric acid or ammonia. This gas residue deports itself differently from the mixture of pure hydrogen, nitrogen, and marsh-gas; with quite active palladium sponge coated with a very thin layer of oxide, no heating-up and no absorption take place.

Upon investigating the behaviour of different gases in the presence of hydrogen toward palladium which contains palladious oxide, it was found that hydrogen could be sharply separated by this reaction —

(1) from marsh-gas and nitrogen,
(2) from ethylene and nitrogen,
(3) from carbon dioxide and nitrogen;

that aqueous vapour and traces of ammonia do not interfere; but that carbon monoxide, large quantities of benzol vapour or alcohol vapour, and traces of hydrochloric acid do interfere.

The reason for this behaviour is that the affinity of the gases last-named for the oxygen of the palladious oxide equals or exceeds that of hydrogen, so that they first burn at the expense of the palladious oxide, and in so doing do not develop enough heat to make the occlusion of the hydrogen possible.

Since we have here to deal with a combustion which, as it happens, takes place at ordinary temperatures, the author believes it must be possible to separate the gases in question with the aid of other metallic oxides and other temperatures, if we could only succeed in raising the temperature slowly and exactly with the help of suitable thermostats, and in keeping the interior of the tube at the same temperature as that prevailing on the outside by diluting the metallic oxides with metals. In this way it might be possible, with the use of simple apparatus, to make the whole gas analysis by fractional combustion. We may call to mind in this connection that in badly performed elementary analyses tarry products distil over feebly glowing copper oxide.

If oxygen is present with hydrogen in the palladium reaction, the oxygen is burned completely to water. But the combustion of the marsh-gas may also take place if the heat rises too much, *i.e.* at temperatures near that of red heat. This rise of temperature may be caused by improperly preparing the palladium in spherical masses, so that the heat evolved during the reaction is then only insufficiently set free by radiation. The difficulties which stand in the way of using palladium, because of the particulars just mentioned, are completely avoided if the absorbable gases are first removed as far as possible, if only an ammoniacal cuprous chloride solution is used, if for the combustion of the last traces of carbon monoxide, ammonia, etc., somewhat more palladium, 4 to 5 gr., is used, and if during the reaction itself the tube with the palladium stands in water of from 90° to 100° temperature. Before using the palladium it is heated, in portions of about 1 g. at a time, nearly to redness upon the cover of a platinum crucible, so that it is covered with a larger quantity of palladious oxide than would be formed by merely leading air over it. The warm water in which the tube stands serves in the beginning to give the gases the temperature necessary to start the combustion, and later it prevents the temperature inside the palladium tube being raised too high by the reaction.

Palladium-black is still more active than the palladium sponge which has been coated with palladious oxide by heating it to redness.

This palladium-black is made by reducing palladious chloride with alcohol in a strongly alkaline solution, the same method being used in preparing platinum-black from platinum chloride. Palladium-black, which is active even in the presence of vapours of hydrochloric acid, is either an oxygen compound of palladium or a mixture of metallic palladium with palladious oxide.

The arrangement of the apparatus for carrying out the reaction is shown in Fig. 77. The gas burette *A* and the gas pipette *B* are joined together by means of the capillary tubes *E* and the tube *H*. This tube *H* is of about 4 mm. internal diameter and 20 cm. total length, and it contains 4 g. of palladium sponge.

The gas pipette upon the stand *G* is filled with water, and its only use is to render it possible to repeatedly pass the gas through the palladium tube.

To determine the amount of hydrogen present in a mixture of hydrogen, nitrogen, and marsh-gas, from which, so far as possible, the absorbable constituents

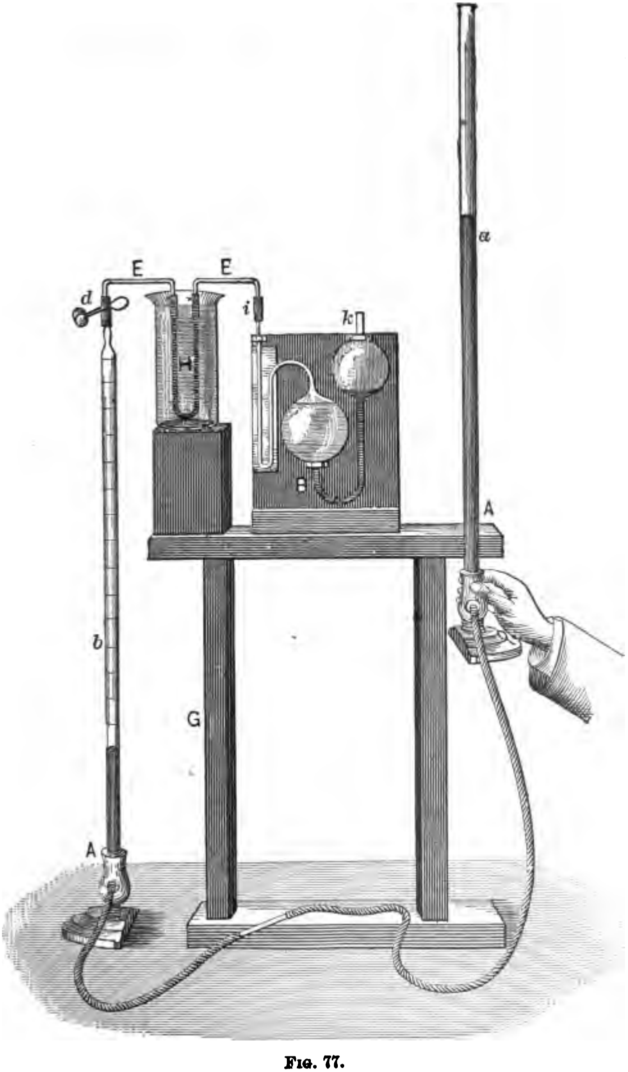
a
E
E
d
i
k
H
A
b
G
A

FIG. 77.

have already been removed, measure the gas in the burette, join it in the manner described to the pipette *B*, which is filled with water nearly to *i*, place the tube *H* in a large beaker, containing warm water of from 90° to 100°, and, after opening the pinchcock *d*, drive the gas three times back and forth through the palladium by raising and lowering the tube *a*. Then replace the hot water with water of the temperature of the room, and lead the gas residue twice back and forth through the tube in order to completely cool the gas. It is in this manner possible to absorb with certainty every particle of hydrogen. Upon drawing the gas so far back into the measuring tube that the water in the pipette again stands near *i*, the difference between the two measurements made before and after the absorption corresponds to the hydrogen + the amount of oxygen in the air enclosed in the U-tube when the apparatus was put together. This air volume, and therefrom its oxygen contents, may be determined with sufficient exactness once for all by closing, with a piece of rubber tubing and glass rod, one side of the tube filled with palladium, cooling the tube to about 9° C. by placing it in cool water, and then, after connecting it by a capillary with a gas burette completely filled with water, warming it to 100° by placing it in boiling water. The expansion of the enclosed air volume corresponds to a difference of temperature of 91°, *i.e.* to a third of the enclosed volume of gas. Since, however, this gas which has been driven over is measured at the temperature of the room, it corresponds to only about a fourth of the volume of the palladium tube. It is important that the palladium contain no water, because the tension of water vapour would cause a considerable error.

The palladium is regenerated after the reaction by first leading air over it, whereby it becomes quite hot; removing any drops of moisture which may collect, so that the palladium may easily be shaken out of the tube in the form of a dry powder; and then superficially oxidising the metal by heating it on the lid of a platinum crucible.

The residue of nitrogen and marsh-gas which remains after the absorption of the hydrogen is burnt by explosion in the manner to be later described.

With the aid of the apparatus here mentioned, the occlusion of hydrogen by palladium may be very strikingly shown; the burette is filled with pure hydrogen from the hydrogen pipette, and is then connected with the pipette by means of a glass tube (Fig. 78) in which 2½ g. of palladium sponge containing some palladious oxide are enclosed. *a* and *b* are capillary, and *c*, which contains the palladium, is about 5 mm. wide.

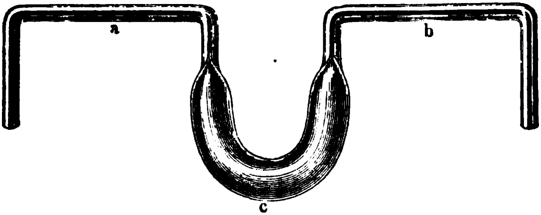

FIG. 78.

Upon leading the hydrogen through the tube, the absorption begins at once without the aid of external heat, and the palladium becomes quite hot; in a very short time, after the gas has been passed but a few times back and to through the palladium, all of the hydrogen disappears. If air is now drawn through the palladium by means of a bottle aspirator or any similar suction arrangement, the hydrogen burns, the palladium being usually seen to glow at some points; the palladious oxide necessary for the reaction is thus formed, and the tube is ready for a repetition of the experiment.

The following analyses serve as illustrations of this method of absorption:—

1. Analyses are here given of two mixtures of nitrogen and marsh-gas made at different times and by the usual method from sodium acetate, and freed by palladium from the hydrogen which is always simultaneously given off. The gases contained, before the absorption with palladium, 6.2 per cent of hydrogen. The analyses were made over mercury with the apparatus for exact gas analysis described in Part I. Chap. IV. *B*, and they showed that it is actually possible to completely free marsh-gas by means of palladium from any hydrogen which it may contain.

The nitrogen of the mixture comes from the air which was not thoroughly driven out during the evolution of the gases, and in the present analysis is of no importance.

The combustion analysis gave the following results:—

I.	Marsh-gas calculated from the contraction	52.45
	“ “ “ carbon dioxide . .	52.3
II.	Marsh-gas calculated from the contraction	50.25
	“ “ “ carbon dioxide . .	50.1

The agreement of these figures is quite sufficient to show that the gases must be regarded as mixtures of marsh-gas and nitrogen free from any noticeable quantities of hydrogen.

2. Analyses here follow of artificial mixtures of hydrogen, marsh-gas, and nitrogen, the marsh-gas being previously freed from any hydrogen it might contain by means of palladium.

(*a*) 27.2 ccm. marsh-gas and nitrogen mixed with 47.5 ccm. hydrogen gave, after absorption with palladium —

27.2 ccm.

(*b*) 27 ccm. marsh-gas and nitrogen mixed with 54.6 ccm. hydrogen gave, after absorption with palladium —

27 ccm.

(*c*) 13.3 ccm. marsh-gas and nitrogen mixed with 41.6 ccm. hydrogen gave, after absorption with palladium —

13.3 ccm.

3. Four analyses of Dresden illuminating gas gave 50.7, 50.6, 50.6, 50.6 per cent hydrogen. The mean of several explosion analyses was 50.5 per cent.

As an example for the calculation, the following analysis of Dresden illuminating gas (April 2, 1879) is given. The direct absorptions gave —

3.5	per cent	carbon dioxide
4.2	"	heavy hydrocarbons
0.2	"	oxygen
10.6	"	carbon monoxide.

The reading after absorption with palladium gave a decrease of volume of 51.5 ccm.

The air contained in the palladium tube was 1.9 ccm., hence the oxygen therein amounted to 0.4 ccm.

Since this oxygen was burned during the reaction, the volume of hydrogen sought is $51.5 - 0.4 = 51.1$ per cent. Of the gas residue of marsh-gas and nitrogen remaining after the hydrogen had been absorbed, 15 ccm. were measured off in a burette and the remainder was kept in reserve in a pipette.

To the 15 ccm. of gas the desired quantity of air was added by lowering the level-tube and opening the pinchcock. The air here added was 82.6 ccm. The mixture was transferred to the explosion pipette, and then as much more air was measured off in the pipette as was probably necessary for the complete combustion of the gas residue, and this air was also brought into the explosion pipette.

For the 15 ccm. of gas residue of marsh-gas and nitrogen 160 ccm. of air were added; in other words, the second portion added amounted to 77.4 ccm.

The gases were thoroughly mixed in the pipette by vigorous shaking, and were then exploded. After the explosion the gas was led into the caustic potash pipette to absorb the carbon dioxide formed, and was then measured.

The residue was more than the burette could hold, and on this account it was measured in two portions. Results: —

First portion	97.5
Second portion	38.0
Total volume after explosion . .	135.5

Hence the contraction was —

$$160 \text{ ccm.} + 15 \text{ ccm.} - 135.5 \text{ ccm.} = 39.5 \text{ ccm.},$$

which corresponds to 13.2 ccm. marsh-gas.

Since the contents of the palladium tube was 1.9 ccm., and the volume of the total residue of marsh-gas and nitrogen 30.4 ccm., the total amount of marsh-gas is given by the proportion —

$$15 : 30.4 + 1.9 = 13.2 : x.$$
$$x = 28.42 \text{ per cent marsh-gas.}$$

The nitrogen is found by subtracting the sum of all the constituents from 100. The result in this case is 2. Hence the composition of the gas is as follows: —

3.5	per cent	carbon dioxide
4.2	"	heavy hydrocarbons
0.2	"	oxygen
10.6	"	carbon monoxide
51.1	"	hydrogen
28.4	"	marsh-gas
2.0	"	nitrogen.

THE ABSORPTION OF HYDROGEN BY POTASSIUM AND SODIUM

Jacquelain[1] has made use of the property of potassium of absorbing hydrogen as a means of separating hydrogen, marsh-gas, and ethylene.

Potassium and sodium can be melted in an atmosphere of hydrogen without absorbing the gas. The absorption begins at 200° and attains its maximum between 300° and 400°; potassium hydride and sodium hydride, substances similar to silver amalgam, are formed. These compounds can be melted in vacuum without decomposition. Heated in vacuum to above 200° they give up hydrogen. At 430° the decomposition in vacuum is complete.

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[1] *Ann. Chim. Phys.* 74, 203.

Potassium absorbs, according to Troost and Hautefeuille, 124.6 volumes of hydrogen; sodium, on the other hand, 23.8 volumes. At 421° the absorption ceases, unless the hydrogen is led in under pressure.

These hydrogen compounds are decomposed by mercury, with formation of potassium or sodium amalgam. These amalgams have no longer the property of absorbing hydrogen.

The author has repeatedly endeavoured to work out a convenient method for making this absorption.

Mercury forms with sodium a solid amalgam, and at the same time sets free again any hydrogen with which the sodium may have united, while petroleum begins to decompose at 400°. Hence we have no confining liquid which may be used to drive the gas completely from one piece of apparatus to another.

The author has sought to use, in a double gas pipette, the alloy of potassium and sodium which is fluid at ordinary temperatures, as confining liquid, but he has finally come to the conviction that this method cannot be employed because of the fact that the slightest trace of oxygen or moisture causes a stoppage of the capillary by the formation of potassium or sodium oxide.

Sodium may conveniently be used for determining hydrogen if the gases are drawn from one vessel to another by means of a small Töpler air-pump of the form used by the author[1] for elementary analysis.

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[1] Fresenius, *Zeitschrift für analytische Chemie*, **17**, **409**.

NITROUS OXIDE (N_2O)

Specific gravity, 1.52269; weight of 1 liter, 1.97023; critical temperature, +35.4°; critical pressure, 75 atmospheres; boiling-point at a pressure of one atmosphere, −87.2°; specific gravity of the liquid gas, 0.9369.

According to Carius, nitrous oxide is quite soluble in water. One volume of water dissolves, at 760 mm. pressure and 20°, 0.670 volume.

The coefficient of absorption is —

$$1.30521 - 0.045362\,t + 0.0006843\,t^2.$$

For alcohol it is —

$$4.17805 - 0.069816\,t + 0.000609\,t^2,$$

and 1 volume of alcohol takes up at 20° 3.0253 volumes N_2O.

Bunsen determines nitrous oxide by combustion with hydrogen and oxyhydrogen gas, the nitrous oxide being thereby split up into water and nitrogen. Since this is a purely volumetric method, it follows that quantities of nitrous oxide which are less than about a fifth of a per cent of a gas mixture cannot be thus determined.

The idea is advanced in different places in the literature of the subject that this method is not exact because of accompanying reactions.

The author has examined the method,[1] and has found that the results are quite satisfactory if the volume of hydrogen is two to three times that of the nitrous oxide, and if such an amount of oxyhydrogen gas is added that to 100 volumes of incombustible gas there will be between 26 and 64 volumes of combustible gas. The combustion is made in the explosion pipette. The decrease of volume is equal to the volume of the nitrous oxide.

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1882, p. 903.

Two volumes of nitrous oxide are made up of 2 volumes of nitrogen and 1 volume of oxygen, and require for combustion 2 volumes of hydrogen. After the combustion, the hydrogen and oxygen have disappeared, but the nitrogen has been set free, hence the contraction is equal to the volume of nitrous oxide sought. Cl. Winkler has proposed[1] to determine nitrous oxide by leading it through a capillary in which a palladium wire is electrically heated to redness; the volume of the gas is thus increased one-half: —

$$2\,N_2O = 2\,N_2 + O_2,$$
$$2 \text{ vol.} = 2 \text{ vol.} + 1 \text{ vol.}$$

This method is, however, not so sharp as the preceding, because the change of volume here amounts to only one-half of the volume of the nitrous oxide, while in the combustion this change is as large as the volume of the N_2O. Special chemical absorbents for nitrous oxide are not known.

On account of the great solubility of nitrous oxide, contact between the gases to be analysed and aqueous solutions must be avoided as far as possible.

At the present time no method exists for detecting traces of nitrous oxide.

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[1] *Anleitung zur chem. Untersuchung der Industrie-Gase*, Part II p. 427.

Nitric Oxide (NO)

Specific gravity, 1.03764; weight of 1 liter, 1.34261; critical temperature, $-93°$; critical pressure, 71 atmospheres; boiling-point at one atmosphere pressure, $-153.6°$; freezing-point, $-167°$; specific gravity of the liquid gas at its critical temperature, 1.039.

The coefficient of absorption for temperatures between 0° and 25° is, according to Carius, for alcohol —

$$0.31606 - 0.003487\,t + 0.00004\,t^2.$$

According to Oscar Lubarsch[1] nitric oxide is absorbed by sulphuric acid of varying concentration in the following amounts: —

1. 100 parts by volume H_2SO_4 absorb 3.5 volumes NO.
2. 100 " " $(H_2SO_4 + 2.5\ H_2O)$ absorb 1.7 vol. NO.
3. 100 " " $(H_2SO_4 + 6.5\ H_2O)$ " 2.0 " NO.
4. 100 " " $(H_2SO_4 + 9.0\ H_2O)$ " 2.7 " NO.
5. 100 " " $(H_2SO_4 + 17.0\ H_2O)$ " 4.5 " NO.
6. 100 " " water absorb 7.2 vol. NO.

The acids mentioned under the numbers from 2 to 5 have the following percentage strength: —

2. 68.5 per cent H_2SO_4.
3. 45.5 " H_2SO_4.
4. 37.7 " H_2SO_4.
5. 24.3 " H_2SO_4.

In the preceding mixtures there are used 2.5, 6.5, 9.0, and 17.0 equivalents of water respectively to one equivalent of concentrated sulphuric acid.

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[1] Oscar Lubarsch's *Inaugural Dissertation*, 1886: "A new nitrometer and the solubility of nitric oxide in sulphuric acid."

Nitric oxide cannot be determined by combustion with hydrogen because, as shown by the researches of Bunsen, the combustion is not a complete one; even when the explosion is quite violent, incomplete combustion to nitrous oxide takes place.

Nitric oxide is determined by absorption with solutions of ferrous salts, which are used in a double pipette. One part of ferrous sulphate is dissolved in two parts of water. The analytical absorbing power is 3.

E. Divers[1] recommends for the same purpose a concentrated solution of sodium or potassium sulphite which has been made alkaline by the addition of some potassium hydroxide. The nitric oxide acting on this reagent forms a hyponitrososulphate, $Na_2N_2O_2SO_3$.

Solutions of potassium hydroxide and sodium hydroxide do not absorb nitric oxide.

The nitric oxide present in a current of gas may be determined by leading the gas through a solution of potassium permanganate acidified with sulphuric acid. The following reaction takes place: —

$$10\,NO + 6\,KMnO_4 + 9\,H_2SO_4 = 3\,K_2SO_4 + 6\,MnSO_4 + 10\,HNO_3 + 4\,H_2O.$$

NITROGEN TRIOXIDE (N_2O_3)

The best absorbent for nitrogen trioxide is concentrated sulphuric acid of at least 1.702 sp. gr.

Nitrogen trioxide is easily absorbed by alkaline solutions with formation of nitrites.

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[1] *Journ. Chem. Soc.* (London), 1899, p. 82.

Potassium permanganate absorbs the gas, and oxidises it to nitric acid. In the presence of sulphuric acid the reaction is—

$$5\,N_2O_3 + 4\,KMnO_4 + 6\,H_2SO_4 = 2\,K_2SO_4 + 4\,MnSO_4 + 10\,HNO_3 + H_2O.$$

NITROGEN TETROXIDE (NO_2)

This gas is actively absorbed by alkaline solutions and by sulphuric acid. By potassium permanganate it is changed to nitric acid.

$$10\,NO_2 + 2\,KMnO_4 + 3\,H_2SO_4 + 2\,H_2O = K_2SO_4 + 2\,MnSO_4 + 10\,HNO_3.$$

AMMONIA (NH_3)

Specific gravity, 0.5889; weight of 1 liter, 0.76199; melting-point, – 78.3°; boiling-point, – 33.7°, specific gravity of liquid ammonia at 0° = 0.6233. 1 volume of water absorbs, according to Bunsen,—

At 700 mm. and 0°	1114.0
“ “	645.2
At 800 mm. and 0°	1128.0
“ “	701.7

Alcohol and ether also absorb considerable quantities of the gas.

Measured quantities of dilute hydrochloric or sulphuric acid are used to absorb the gas, and the amount of ammonia is determined by titrating back with a standard solution of an alkali.

If a direct determination is not possible, as, for instance, in gases containing large amounts of tar, the ammonia may be absorbed in sulphuric acid, and the nitrogen present may then be set free, and measured in a Knop azotometer.

This simple and very exact method has been further worked out by Wolf, Dietrich, P. Wagner, and F. Soxhlet.[1] It is based upon the action of alkaline hypobromites upon salts of ammonia, all nitrogen present being set free.

$$3\,NaBrO + 2\,NH_3 = N_2 + 3\,H_2O + 3\,NaBr.$$

If urea is present, its nitrogen is also set free.

The apparatus necessary for making this determination is described on p. 72 (Fig. 41).

In carrying out the analysis, the amount of nitrogen actually given off in the apparatus under the experimental conditions is determined by using a normal ammonium chloride solution; in the second experiment, the liquid in question is put into *o*, Fig. 41. The difference between the found and calculated amount of nitrogen in the first experiment gives a correction, which is introduced in the calculation of the results from unknown amounts.

METHYL-AMINE ($NH_2.CH_3$)

Specific gravity, 1.13.

1	volume of water	absorbs	at 12°	1040	volumes.
1	"	"	" 25°	955	"

It condenses at a temperature somewhat under 0°. It is absorbed by acids.

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[1] Fresenius, *Quantitative Analyse*, 6th ed. Part II, pp. 681 and 715.

CARBON DIOXIDE (CO_2)

Specific gravity, 1.51968; weight of 1 liter, 1.96633; critical temperature, 31°; critical pressure, 77 atmospheres; boiling-point at pressure of 1 atmosphere, – 79.3.

According to Bunsen and Pauli, 1 volume of water takes up

$$1.7967 - 0.07761\,t + 0.0016424\,t^2.$$

1 ccm. of sulphuric acid (sp. gr. = 1.78) dissolves at 14° C. and 816.4 mm. pressure 1.16 ccm. of carbon dioxide.

To absorb carbon dioxide either potassium hydroxide or barium hydroxide is used.

For volumetric determinations a solution of 1 part of commercial caustic potash in 2 parts of water is employed. Analytical absorbing power, 40 ccm. carbon dioxide. This solution is put into the simple pipette for solid and liquid reagents (Fig. 32), the cylindrical part *C* being first closely filled with very short rolls of iron wire-gauze. The gauze has a mesh of 1 to 2 mm., and the rolls are from 1 to 2 cm. long and about 5 mm. thick.

When the per cent of carbon dioxide is not too high, it can be completely absorbed by simply passing the gas once into the pipette. The complete manipulation does not take one minute.

Since a 33⅓ per cent solution of caustic potash is quite viscous, so much of the reagent remains hanging on the gauze when the gas is introduced that on the one hand the absorption of the carbon dioxide takes place at once, and on the other hand the simultaneous absorption of oxygen, caused by the oxidation of the iron, is impossible, because the gauze is completely protected by the solution from the action of the air, as repeated experiments have shown.

The wire-gauze has a further advantage. It cools the warm gases at once down to the temperature of the room, so that the absorption of the carbon dioxide formed in the combustion of marsh-gas (see later) may also be very suitably made in the carbon dioxide pipette.

Small quantities of carbon dioxide are best determined by absorption in a solution of barium hydroxide and titration with oxalic acid.

CARBON MONOXIDE (CO)

Specific gravity, 0.96709; weight of 1 liter, 1.25133; critical temperature, – 141°; critical pressure, 35 atmospheres; boiling-point under pressure of 1 atmosphere, – 190°; freezing-point, – 207°. 1 volume of water dissolves, according to Bunsen, —

$$0.032874 - 0.00081632\,t + 0.000016421\,t^2$$

volume of carbon monoxide; hence at

20°, 0.02312.

According to Carius, alcohol dissolves between 0° and 25°, 0.20443 volume CO.

For absorbing carbon monoxide, either an ammoniacal or a hydrochloric acid solution of cuprous chloride is used.

The hydrochloric acid solution of cuprous chloride may be prepared, according to Winkler, by adding a mixture of 86 g. of copper oxide and 17 g. of finely divided metallic copper to 1086 g. of hydrochloric acid (sp. gr. = 1.124), the mixture being slowly introduced and the acid frequently stirred. The copper powder is best prepared by the reduction of copper oxide with hydrogen. After this mixture has been introduced into the acid, a spiral of copper wire reaching from the bottom of the bottle up to its neck is inserted and the bottle is closed with a soft rubber stopper. The solution is dark in the beginning, but upon standing it becomes wholly colourless. In contact with the air, however, it again turns dark brown, and some cupric chloride forms.

The analytical absorbing power of the solution is 4 ccm. of carbon monoxide.

Another method somewhat more rapid and convenient than that just described is given by Sandmeyer.[1]

25 parts of crystallized copper sulphate and 12 parts of dry sodium chloride are placed in 50 parts of water and heated until the copper sulphate dissolves. Some sodium sulphate may separate out at this point, but the preparation is continued without the removal of this salt. 100 parts of concentrated hydrochloric acid and 13 parts of copper turnings are then added and the whole is boiled in a flask until decolourised. To avoid excessive evaporation it is desirable to insert in the neck of the flask a tall condensing tube or an upright condenser. The addition of platinum foil to the contents of the flask will facilitate reduction. The solution should be

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[1] *Berichte der deutschen chemischen Gesellschaft* **17**, 1633.

kept in bottles which are filled up to the neck and are closed by rubber stoppers.

The ammoniacal solution of cuprous chloride is prepared (the amounts here given make 200 ccm.) by dissolving 10.3 g. of copper oxide in 100 to 200 ccm. of concentrated common hydrochloric acid, and then allowing the solution to stand in a flask of suitable size, filled as full as possible with copper wire or copper wire-gauze, until the cupric chloride is reduced to cuprous chloride, and the solution is completely colourless. The clear hydrochloric acid solution thus prepared is poured into a large beaker glass or cylinder containing 1½ to 2 liters of water, to precipitate the cuprous chloride formed. After the precipitate has settled, the dilute hydrochloric acid is poured off as completely as possible, the cuprous chloride is then washed into a 250 ccm. flask with about 100 to 150 ccm. of distilled water, and ammonia is led into the solution, which is still slightly acid, until the liquid takes on a pale blue colour. Since the tension of very concentrated ammonia solutions renders the absorption difficult, no more ammonia than is necessary should be added. While the ammonia is being led in, it is well to protect the contents of the flask from the oxidising influence of the air. This may be done by providing the flask containing the cuprous chloride to be dissolved, with a double-bored stopper through one opening of which passes the delivery tube from the ammonia flask, while through the other opening is inserted a bent glass tube that dips into a little mercury. If a flask with a funnel-tube is used for the evolution of ammonia, hydrogen may first be led through this tube, and the apparatus be thus completely freed from air. For the evolution of ammonia about 200 ccm. of a concentrated ammonia solution of 0.9 sp. gr. is used.

The solution of cuprous chloride thus prepared is diluted with water to 200 ccm., and, since the hydrochloric acid was not entirely washed out, there is of course some ammonium chloride present. 100 ccm. contains 7.3 g. of cuprous chloride.

The analytical absorbing power of this solution is 6 ccm. of carbon monoxide.

It is quite impracticable to use more dilute solutions of cuprous chloride.

The following method for the preparation of an ammoniacal solution of cuprous chloride will be found convenient. 1 liter of the hydrochloric acid solution prepared by the Winkler method given above or 1500 cc. of the Sandmeyer solution is poured into about 5 liters of water, and the resulting precipitate is transferred to a stoppered measuring cylinder containing about 320 ccm. and upon which there has previously been marked the height at which 62 ccm. of liquid would stand. After about two hours the precipitate and liquid which is above this 62 ccm. mark is drawn off by means of a siphon and 7.5 per cent ammonium hydroxide is added up to the 320 ccm. mark, that is, to the top of the cylinder. The stopper is inserted, the cylinder is well shaken, and it is then allowed to stand for several hours. A solution prepared in this manner has so slight a tension that the latter may in nearly every case be neglected.

If, after the absorption of the carbon monoxide in a gas mixture, the hydrogen is to be determined with palladium, the ammoniacal solution must be used. If the amount of carbon monoxide alone is to be ascertained, the hydrochloric acid solution may be employed with equally good results. These solutions of cuprous chloride are used in the double pipette (Fig. 33).

H. Drehschmidt[1] has shown, however, that the union of carbon monoxide with cuprous chloride is so feeble that upon shaking a solution which has taken up any considerable quantity of carbon monoxide, this gas is again given up in an atmosphere free from carbon monoxide. For this reason two pipettes are used in the absorption, one pipette containing a frequently used, the other a but slightly used, solution of cuprous chloride. In the absorption, the gas in question is first shaken for two minutes with the first-mentioned solution, and is then transferred to the second pipette containing the but slightly used solution, and is shaken three minutes therein. According to Drehschmidt, the ammoniacal solution is to be preferred to the hydrochloric acid one.

Solutions of cuprous chloride have no considerable tension, so that this may be disregarded in analyses which are to give only approximate results, or in which no great accuracy is necessary. In exact determinations, however, the gases which have been in contact with the reagent must be freed from the gaseous hydrochloric acid or from the ammonia; this can be brought about in the burette itself, or in a pipette filled with distilled water.

The solutions of cuprous chloride are thin, and they flow readily; hence it is unadvisable to make the absorption in the double pipette for solid and liquid reagents (Fig. 34), in which the cylinder *a* has been filled with copper wire-gauze, for the absorption is not here effected, as with carbon dioxide, by simply leading the gas once into the pipette; on the contrary, it can be brought about only after some time by frequently repeating this operation.

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[1] *Berichte der deutschen chemischen Gesellschaft,* **20**, 2344; **20**, 2752; and **21**, 2158.

The solutions of cuprous chloride are absorbents not only for carbon monoxide and acetylene, but also for ethylene — a fact which is not taken into account in a number of gas analyses lately published, and the disregard of which must of course lead to wholly useless results.

The author was unable to find any notice of this particular in the existing literature, and by the recurrence of an error in an analysis of illuminating gas he was led to investigate the behaviour of cuprous chloride toward ethylene. He at first believed that marsh-gas was somewhat soluble in cuprous chloride, but further experiments showed that this was not the case.

To study the action of ethylene toward cuprous chloride, 25 parts by weight of absolute alcohol were mixed with 150 parts by weight of concentrated sulphuric acid, and the gas given off upon careful heating was passed, first through an empty bottle, and then through concentrated sulphuric acid and through several wash-bottles filled with a concentrated solution of potassium hydroxide. After the evolution of gas had gone on for an hour, the gas was collected in a small glass gasometer over a strongly alkaline solution of pyrogallol, and was analysed after standing for several days. 91.3 per cent of the gas was absorbable by concentrated sulphuric acid.

Another portion of the gas, brought together with a hydrochloric acid solution of cuprous chloride, gave 94.3 per cent of absorbable gas.

Another sample of ethylene prepared by the same method gave, in two experiments with hydrochloric acid cuprous chloride, 94.5 per cent of absorbable constituents.

In two experiments with ammoniacal cuprous chloride, 95.0 per cent of absorbable constituents.

The last four analyses were not made in pipettes, but in the simple gas burette with unsaturated reagent. The difference in the results is caused by the different solubility of nitrogen in ammoniacal and hydrochloric acid cuprous chloride ; and it is as large as it is because the residual 5 ccm. of gas in the analysis came into intimate contact with 95 ccm. of unsaturated absorbing liquid.

In the method of preparing ethylene described above, some carbon is always separated, and this, upon being heated with sulphuric acid, gives off carbon monoxide in addition to sulphur dioxide and carbon dioxide The presence of the carbon monoxide completely explains why the cuprous chloride absorbed 3 per cent more gas than the fuming sulphuric acid.

Certain analytical data indicate that the heavy hydrocarbons are not equally absorbable by the reagent. Ethylene appears to be absorbed with especial ease. It remains, therefore, to ascertain whether cuprous chloride itself cannot be used for separating the heavy hydrocarbons.

Preliminary experiments showed further, that the gases not absorbable by cuprous chloride are much more soluble in this reagent than in other absorbing liquids. This fact shows that, to obtain accurate results, a cuprous chloride solution which has been saturated with the gases but slightly soluble in it must unquestionably be used.

In the three determinations, given later, of carbon monoxide in an illuminating gas from which the carbon dioxide, heavy hydrocarbons, and oxygen had been absorbed, 8.6 and 8.5 per cent of carbon monoxide was found with unsaturated reagent, and 8.1 per cent with reagent which had been saturated by repeated use, but which still possessed high absorbing power.

These experiments showed further that the cuprous chloride solution is not suited to the absorption of oxygen, since complete absorption is attained only after shaking for a very long time. The gases to be treated with this reagent must on this account be free from oxygen.

The author has also found that the hydrochloric acid solution of cuprous chloride is not changed by petroleum, so that this reagent may be kept under petroleum in a bottle having at the bottom a tubulus and stopcock; the bottle should be completely filled and tightly stoppered. If, after some cuprous chloride has been taken out, the bottle is kept full of petroleum and tightly closed, the solution does not change in strength.

In May, 1885, Mr. Karl Markel, chemist of the Ammonia-soda Works at Winnington, England, called the author's attention to the fact that in the absorption of carbon monoxide with cuprous chloride, the gas volume at times did not decrease, but on the contrary became considerably greater. He sent a number of analyses of generator gases in confirmation of his statement. In none of these analyses were the heavy hydrocarbons determined either by fuming sulphuric acid or any other reagent, so that it was surmised that these gases might be the cause of the irregularity. Experiments have borne out this assumption, and have shown that even when the determination of the heavy hydrocarbons is of no importance for the analysis, they must, nevertheless, be removed before the carbon monoxide is absorbed with cuprous chloride.

If ethylene is absorbed with cuprous chloride, and this solution is then used for the absorption of carbon monoxide, a certain quantity of ethylene is set free, so that the results of the analysis are of course erroneous. If the same solution of cuprous chloride is used for a large number of absorptions, the case may arise that the gas volume does not decrease when the carbon monoxide is absorbed, but on the contrary is increased by the ethylene set free. It is obvious that an increase of volume may also be caused by carbon monoxide being set free in the manner mentioned by Drehschmidt.

Cl. Winkler[1] has found that if palladious chloride be added to solutions of cuprous chloride in hydrochloric acid, ammonium chloride, or sodium chloride, then these solutions, if they have absorbed carbon monoxide, give upon dilution with water a precipitate of metallic palladium, the carbon monoxide being at the same time oxidised to carbon dioxide.

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[1] Fresenius, *Zeitschrift für analyt. Chemie*, **28**, 269.

F. P. Treadwell and H. N. Stokes[1] have shown that carbon monoxide can be completely absorbed with fuming nitric acid, if the two are shaken together for quite a long time (25 minutes).

Small quantities of carbon monoxide may be detected by means of blood. H. W. Vogel[2] was the first to use the well-known spectrum reaction of blood impregnated with carbon monoxide, as a means of finding small amounts of the gas. This reaction is of especial significance, because the carbon monoxide cannot be confounded with another gas — a fact which, on account of the highly poisonous character of the substance, is of great importance in analyses undertaken from a sanitary standpoint.

To detect carbon monoxide, Vogel directs that a 100 ccm. bottle, filled with water, be emptied in the room containing the gas, and that 2 to 3 ccm. of blood, highly diluted with water, and showing only a very faint red colour, yet still giving the well-known absorption bands of oxyhæmoglobin (see Fig. 79, spectrum No. 2) in a column as thick as a test-tube, be poured into the bottle and shaken for some minutes. When carbon monoxide is present, the blood at once takes on a rose colour, the absorption bands shift slightly toward the violet, and the spectrum of carbon monoxide hæmoglobin appears (Spectrum No. 3). When a few drops of strong ammonium sulphide are added to this solution the absorption bands do not disappear, but on the contrary, maintain their position. If, however, no carbon monoxide has come into contact with the blood, the bands due to the oxyhæmoglobin (Spectrum No. 2) disappear and are replaced by a broad and weakly defined band (Spectrum No. 4).

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1888, p. 3131.

[2] *Ibid.* **11**, 235; also **10**, 792.

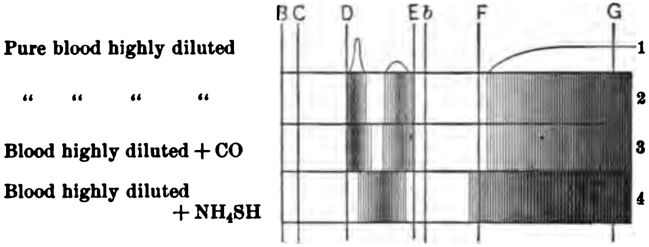
B C D E b F G
Pure blood highly diluted
1
" " " "
2
Blood highly diluted + CO
3
Blood highly diluted + NH_4SH
4

Fig. 79.

Vogel states that amounts down to 0.25 per cent can be clearly detected, but that the delicacy is not increased by using greater volumes of air.

The author found by experiment that it was not possible, in a Liebig potash-bulb or by shaking, to completely remove very small amounts of carbon monoxide from a gas mixture by means of an exceedingly dilute solution of blood, such as Vogel employs; and he also found that concentrated solutions of blood could not be used because they foam so much. He was thus led to the idea that by using living animals, whose lungs would furnish an absorption apparatus of incomparable completeness and admit of the use of undiluted blood, it might be possible to still further increase the delicacy of the reaction.

This supposition was proved correct by the experiments which follow, and it led to a more delicate method for detecting carbon monoxide.

Mice were used in the work, and they were exposed to the action of the gas to be tested for carbon monoxide by placing them between two funnels joined together at the mouths by means of a broad band of thin rubber. The ends of the funnels were connected to the gasometers and absorption apparatus by pieces of rubber tubing.

To bring the mouse, without hurting it, into this simple apparatus, the animal is first dropped into a large and wide glass cylinder. It is then covered with one of the funnels, a glass plate is slipped under the funnel, and the mouse is lifted out. The mouth of the second funnel is then brought opposite that of the first one, the glass plate is drawn out, and the funnels are joined together by the rubber band.

Mixtures of air and carbon monoxide were used in the experiments. The carbon monoxide was made with great care, either from potassium ferrocyanide and sulphuric acid, or from oxalic acid and sulphuric acid, and was washed with a sodium hydroxide solution. The lighter carbon monoxide was led into the air from below, and the mixture was allowed to stand and diffuse for at least twelve hours.

The current of gas was so regulated that 10 liters of gas passed through the apparatus in from one to two hours, and the gases coming from the funnels contained from 0.3 to 2.8 per cent of carbon dioxide, resulting from the respiration of the mouse. Frequently repeated analyses showed, however, that this carbon dioxide did not usually rise above 1 per cent, so that it was impossible for it to cause any seriously injurious results.

In some experiments also, as is described in detail below, a Liebig potash-bulb filled with a fresh blood solution, which was highly diluted according to Vogel's directions, was placed either before or after the animal.

The mice were killed by immersing the funnels in water, and a considerable quantity of blood was obtained by cutting them in two in the region of the heart.

The detection of the carbon monoxide hæmoglobin was always carried out with a freshly prepared solution of colourless ammonium sulphide; and to control the results, fresh blood of the same dilution and free from carbon monoxide was treated with the same amount of ammonium sulphide. To obtain this fresh blood a mouse which had not been in contact with carbon monoxide was killed shortly before the experiment.

To still further control the results, the author also used in most of the experiments freshly prepared ammonium ferrous tartrate, with the same success as with the ammonium sulphide. But the preference must be given to the colourless ammonium sulphide, because, when that is used, a difference in the colours of the reduced solutions when traces of carbon monoxide are present, is quite easily distinguishable even without the aid of the spectroscope. The liquid containing the carbon monoxide hæmoglobin is more distinctly red in colour.

A Vogel "universal spectroscope," made by Schmidt and Haensch, was used for observing the spectra.

Experiment 1. — The gas contained 0.022 per cent carbon monoxide. Before the animal there was placed an absorption apparatus containing blood.

The mouse showed no symptoms of poisoning. Experiment was stopped at the end of three hours.

Carbon monoxide could be detected neither in the mouse nor in the interposed blood.

Experiment 2. — Gas contained 0.032 per cent of carbon monoxide. No absorption apparatus containing blood was placed before the animal.

The mouse showed no symptoms of poisoning. Experiment was stopped at the end of three hours.

The blood of the mouse gave a weak but unmistakable reaction for carbon monoxide.

Experiment 3. — Gas contained 0.032 per cent of carbon monoxide. Only an absorption apparatus containing a dilute blood solution was used.

Carbon monoxide could not be detected. Considerable albumen was coagulated, so that the solution, which previously had been clear, was now turbid.

Experiment 4. — Gas contained 0.043 per cent of carbon monoxide. The mouse showed no symptoms of poisoning. Experiment was stopped at the end of four hours. Distinct reaction for carbon monoxide. Even without the aid of the spectroscope, the presence of carbon monoxide could be clearly recognised from the red tone of the reduced blood.

Experiment 5. — Gas contained 0.067 per cent carbon monoxide. An absorption apparatus containing blood was interposed before the animal.

After half an hour slight symptoms of poisoning — difficult respiration — could be seen. After three hours the experiment was stopped.

In the mouse the carbon monoxide could be plainly detected; the blood solution also gave the reaction, but much more faintly.

Experiment 6. — Gas contained 0.0593 per cent of carbon monoxide. An absorption apparatus containing blood was placed after the mouse.

After half an hour unmistakable symptoms of poisoning showed themselves — the mouse breathed with difficulty and lay exhausted on its side. The experiment was stopped at the end of 47½ minutes. Carbon monoxide in the animal could be clearly recognised, but less plainly in the blood solution.

Experiment 7. — Gas contained 0.127 per cent of carbon monoxide. An absorption apparatus containing blood was placed before the animal.

At the end of only seven minutes there were strong symptoms of poisoning. The interposed blood solution, as well as the blood of the mouse, gave the reaction for carbon monoxide at the end of two hours.

Experiment 8. — Gas contained 2.9 per cent of carbon monoxide. In from one to two minutes the mouse died with convulsions. The blood gave a strong carbon monoxide reaction.

This last experiment shows vividly the frightfully poisonous action of carbon monoxide, for a few cubic centimeters of the still very dilute carbon monoxide suffice to produce at once strong symptoms of poisoning in a mouse.

Taking the results as a whole, we see —

(1) That when large volumes of gas (at the least 10 liters) are used, amounts of carbon monoxide down to 0.05 per cent can be easily and certainly detected either by using dilute blood or a living animal (a mouse).

(2) That the limit of the test lies at about 0.03

per cent when a mouse is used, and with dilute blood at about 0.05 per cent.

(3) That decided symptoms of poisoning are observed from 0.05 per cent upward.

The author is accordingly of the opinion that, to examine the air of a room for carbon monoxide, either the Vogel test must be used, a few cubic centimeters of very dilute blood being placed in an absorption apparatus and 10 liters of air, at the least, being led through it, or, as is more convenient in many cases and also more delicate, that a mouse placed in an ordinary wire trap be allowed to breathe the air of the room for some hours, and the blood of the animal be then examined.

Vogel,[1] and, later, Gustav Wolffhügel, in his very interesting article upon "carbon monoxide and cast-iron stoves,"[2] state that in their opinions quantities of carbon monoxide smaller than 0.25 per cent — the limit of the delicacy of the Vogel test when 100 ccm. of air is used — may be disregarded from a hygienic standpoint, and they would regard the presence of traces of carbon monoxide in the air of a room in the same light as one looks upon the presence of organic substances, of nitric acid, etc., in drinking water, or of carbon dioxide in the atmosphere. But, in the opinion of the author, this view cannot be accepted when we take into consideration the foregoing experiments, and the fact also that carbon monoxide does not belong, as does carbon dioxide, to the unavoidable constituents of the air of a room. Moreover, in inspecting heating arrangements, the presence of any carbon monoxide should, from a sanitary standpoint, be regarded as inadmissible, this judgment being wholly independent of the statement that there must be a lower limit at which carbon monoxide has no poisonous action on the human organism.

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[1] *Berichte der deutschen chemischen Gesellschaft*, **11**, 236.

[2] *Zeitschrift für Biologie*, **14**, 506.

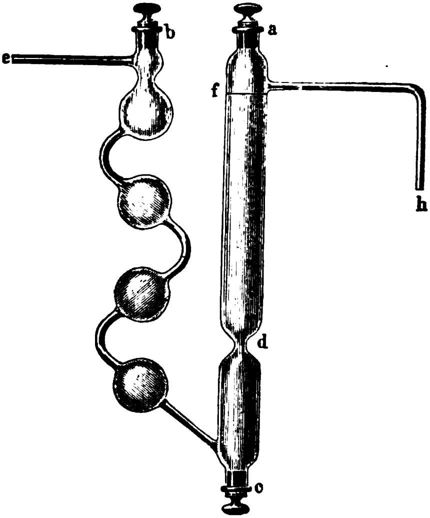

Fig. 80.

C. H. Wolff[1] has constructed a very effective absorption apparatus adapted to the use of small amounts of blood. He describes it as follows:—

"It corresponds essentially to the De Koninck modification of Mitscherlich's absorption apparatus, the difference being that at *a*, *b*, and *c* (Fig. 80) the tubes are closed by ground-glass stoppers, and that the cylinder is narrowed at *d*. In filling the apparatus, a little wad of glass-wool is inserted into *d* from above, and gently pressed into place, and the remainder of the tube as far as *f* is then filled with moderately fine powdered glass. This powdered glass is about as fine as ordinary gunpowder. It is freed from any fine powder and dust by sifting, and is then digested with hydrochloric acid, and carefully washed and dried. The great extent to which the size of these grains adds to the power of absorption through increase of surface is shown by the interesting researches of Dr. Soyka in Prague, upon the influences of the soil upon the decomposition of organic substances and the formation of nitric acid. The glass powder is moistened with water from above; strong suction is then applied at *e* by attaching an aspirator thereto, and the excess of water which is thus drawn off from the powdered glass is removed at *c*. 2 ccm. of dilute blood (1 : 40) is then allowed to drop from above, from a pipette, upon the moistened glass, *a* is closed, and by gently blowing into *h* with the mouth a uniform distribution of the blood solution throughout the column of powdered glass down to the glass-wool is effected. The apparatus is ready for the absorption, and it is now connected either at *e* with the aspirator or at *h* with the bottle, depending upon whether the 10 liters of air are to be drawn through or driven through. An ordinary bottle containing somewhat more than 10 liters is very well suited to the taking of the sample of the air to be examined. This bottle is supplied with a double-bore rubber stopper, through the openings of which pass two glass tubes bent at right angles above the stopper. One of these tubes ends just below the stopper, and the other reaches to the bottom of the bottle. Pieces of rubber tubing of sufficient length, and closed by Bunsen screw-pinchcocks, are slipped over the free ends of both tubes. Since the bottle holds more than 10 liters it is provided near the bottom with a mark, from which point up to the stopper the capacity is exactly 10 liters. To fill the bottle with the air to be examined, it is filled completely with water, and this is then run out through the rubber tube which is connected to the longer glass tube, and which acts as a siphon. When the water has fallen to the 10 liters mark both pinchcocks are closed. To pass the air through the absorption apparatus, the same rubber tube which has acted as a siphon is attached to a bottle filled with water, and standing higher than the first bottle, and the other rubber tube is connected with the absorption apparatus. The current of air, which may be very exactly regulated by means of the screw-pinchcock, must pass through the absorption apparatus very slowly—on an average, 1000 ccm. in twenty to twenty-five minutes. To be able to observe and regulate the passage of the air through the apparatus, 2 to 3 ccm. of water are run in at *b* after the powdered glass has been moistened with the blood solution. When the experiment is ended, this water is let out at *c*. Any burette holder is suited to holding the absorption apparatus; a Vogel 'universal stand' is also well adapted to the purpose. If it be desired to draw the air of the room in question directly through the apparatus, — a proceeding which is, however, not to be recommended because of the possible change in the composition of the air during the long duration of the experiment, — the end *h* is joined by a cork to a so-called calcium chloride cylinder containing pieces of pumice-stone moistened with water. The air enters the cylinder from below, becomes saturated with moisture, and then passes into the absorption apparatus. When 10 liters of air have been led through, in one manner or the other, the stopper at *c* is removed to let out the water. A small test-tube, upon which is a mark for 3 ccm., is then placed under *c*, the stopper at *a* is removed, and pure water is slowly dropped from a pipette upon the powdered glass. The blood solution is thus gradually displaced, and the washing is continued in this manner until the liquid in the test-tube amounts to 3 ccm. The tube is then taken away, several cubic centimeters of water are allowed to flow through the powdered glass, all the stoppers are inserted, *e* is connected with the aspirator, and when the excess of water has thus been removed the apparatus is ready for another experiment.

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[1] *Correspondenzblatt des Vereins analytischer Chemiker*, 1880, **3**, 46.

"The same powdered glass was used for from 50 to 60 determinations without it being necessary to renew it. The absorption apparatus contained originally 2 ccm. of dilute blood 1 : 40; hence the 3 ccm. now in the test-tube have a concentration of 1 : 60.

"Small rectangular bottles, with flat sides which are 0.5 cm. and 1 cm. wide, are very well suited to holding the blood solution for the observations with the spectroscope: these little bottles hold about 1.5 ccm. of solution, and are closed with carefully ground stoppers. One of these bottles is filled with the blood solution used in the experiment, and a second bottle is filled with the original blood solution, also diluted to 1 : 60. One drop of ammonium sulphide is added to the contents of each bottle; the bottles are shaken, and after half an hour the spectra of the two solutions are examined, preferably by lamplight, with a delicate pocket spectroscope.

"When the method is carried out as just described, it admits of a comparison of the two blood solutions under quite similar and at the same time the most favourable conditions as regards the concentration, the thickness of the observed column of liquid, the reducing agent, and the duration of the experiment. With respect to the lowest limit of the possible and certain detection of carbon monoxide in atmospheric air, I have, after many experiments, come to the same result as Hempel, viz., 0.03 per cent. At this concentration both bands are still distinctly recognisable. When the air contains less carbon monoxide, about 0.02 per cent, the presence of the gas is shown merely by a somewhat stronger absorption in the absorption spectrum, which now appears at *D* as a broad band, the maximum absorption of the reduced blood solution lying toward *E*. This observation is the last evidence, as Jäderholm has already stated in his admirable paper upon the lego-medical diagnosis of carbon monoxide poisoning, p. 22, which shows that some carbon monoxide is still present.

"It is very desirable to possess for these experiments a solution of blood which is clear, and which will keep for a long time, and the method proposed by Jäderholm (p. 30 of his article) answers the purpose excellently. He mixes together equal volumes of blood freed from fibrine, and of cold saturated borax solution. The addition of the borax prevents putrefaction and does not change the spectroscopic properties of the blood, and reduction and combination with oxygen or carbon monoxide take place in the same manner as in fresh blood or hæmoglobin solution. The hæmoglobin gradually dissolves in the liquid, and, beginning at the bottom and proceeding upward, the solution takes on a deep dark red colour. Such a solution of the colouring matter of blood in borax remains clear for months, and does not need to be filtered before being used for the spectroscopic examination. I have used this solution exclusively for my experiments, the desired concentration of 1 : 40 being obtained by mixing 1 ccm. of the solution with 19 ccm. of water. Even in this dilution, the solution will keep for several days.

"The permanence of the carbon monoxide reaction in this dilution, when the solution is kept in the small and tightly closed absorption bottles, is quite remarkable. I have kept solutions with 0.03 per cent and 0.05 per cent, together with the comparing solutions, for over three months without the reaction becoming less distinct.

"I will mention one other experiment which is of interest as serving to call attention to certain necessary precautions in the examination of the air of rooms filled with coal-gas.

"After the delicacy of the method had been proved by many experiments, it remained to test it also in a practical manner. For this purpose a small stove filled with burning charcoal was placed in a closed room in my laboratory, and the doors and openings into the chimney were closed. Into the room was passed a glass tube with a funnel-shaped mouth. This tube was connected with a Mitscherlich bulb apparatus filled with water for washing the gas, and this was joined to a 10-liter bottle which aspirated the air. At the same time a 100-ccm. bottle, filled with water, was emptied in the same room, 3 ccm. of very dilute blood was put into it, and the walls of the bottle were rinsed for three to four minutes with this solution. Both experiments were begun after the charcoal had burned in the small room for about half an hour, at which time the air was stifling and of a peculiar acid odour, while what is commonly termed coal-gas was present in large amounts. Nevertheless the Vogel test showed no trace of carbon monoxide, and, moreover, my method, which had shown itself at other times to be so delicate, failed me completely, because all the colouring matter of the blood in the powdered glass was destroyed in a short time and the solution was consequently decoloured. It was evident, as was already shown by the slight bluish appearance in the bottle, that in spite of the interposed wash-bottle there had passed over those acid products of the decomposition and dry distillation of coal (perhaps phenol), which form when the coal is not completely burned, and which Hünefeld, in his work upon the legal tests for blood and carbon monoxide in blood,[1] has described in detail and has attempted to isolate.

"The bottle containing the remainder of the gas and some water was shaken several times and was allowed to stand until the next day; these substances were then absorbed, and 5 liters of the air still remaining in the bottle sufficed to give undoubted evidence of the presence of carbon monoxide. It would, however, be advisable to interpose a cylinder filled with coarse and moist powdered glass, and another filled with freshly slaked lime, as Wolffhügel has recommended."

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[1] Leipsic, 1875, p. 40.

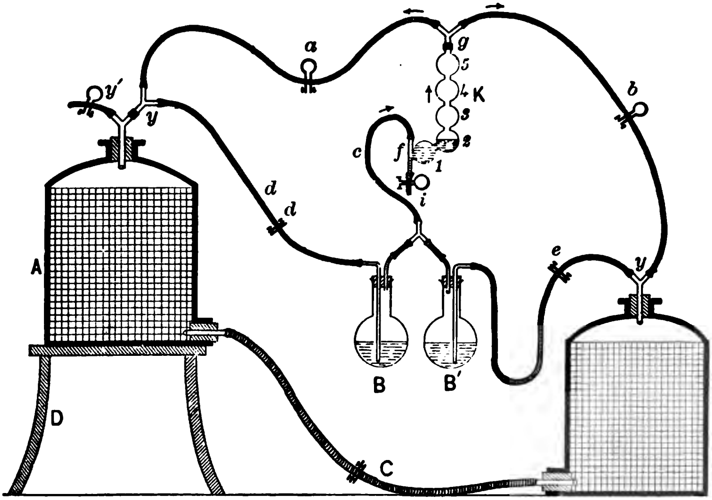

FIG. 81.

S. Kostin has found[1] that it is possible to detect one part of carbon monoxide in 40,000 parts of air. He first removes the oxygen of the air by passing the latter through 3 liters of a saturated solution of ferrous sulphate to which 1 liter of strong ammonium hydroxide has been added. The solution is placed in an aspirator bottle that is filled with iron gauze (see *A*, Fig. 81). 4 liters of this solution, which contains much undissolved ferrous hydroxide, is able to absorb the oxygen in from 80 to 100 liters of air. The volume of air under examination is passed from one such aspirator into another through an interposed blood solution contained in *K*, until all oxygen has been removed. To prevent ammonia vapor from coming into contact with the blood, the air is first caused to pass through wash-bottles *B* and *B'* containing oxalic acid. It takes about two hours to completely remove the oxygen from the volume of air above mentioned.

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[1] *Archiv für die Gesammte Physiologie*, **83** (1901), 572.

A number of chemists have busied themselves with the investigation of various methods for detecting the presence of carbon monoxide in blood. Of all the methods that have been proposed, Kostin considers that suggested by Kunkel to be the best. The blood is here diluted with 10 volumes of water and an equal volume of a 3 per cent tannin solution is then added. If the blood contains carbon monoxide, a reddish precipitate is formed, while with normal blood the precipitate is dark brown. These colour reactions become especially distinct after five or six hours.

C. de la Harpe and Reverdine[1] first used the reaction between iodine pentoxide and carbon monoxide for the detection of the latter substance, the reaction being $I_2O_5 + 5\,CO = 2\,I + 5\,CO_2$, and Nicloux[2] and Gautier[3] employed this reaction for the quantitative determination of carbon monoxide. Kinnicutt and Sanford[4] have shown that this method can be used for the detection of very small amounts of carbon monoxide not only in air, but also in illuminating gas, provided the latter is first passed through two U-tubes, one containing sulphuric acid and the other small pieces of potassium hydroxide. The iodine set free in the reaction is titrated with a $\frac{N}{1000}$ solution of sodium thiosulphate. By this method it is possible to detect one part of carbon monoxide in 40,000 parts of air when using as small a volume of air as 1 liter.

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[1] *Chem. Ztg.* **12** (1888), 1726.

[2] *Compt. rend.* **126**, 746.

[3] *Ibid.*, **126**, 931.

[4] *J. Am. Chem. Soc.* **22** (1900), 14.

Carbon monoxide may also be detected with sodium palladium chloride, metallic palladium being thrown down and the gas being changed to carbon dioxide. But palladium chloride is also decomposed by a large number of organic substances, and mistakes may arise from this cause.

METHANE (CH_4)

Marsh-gas — Fire-damp

Specific gravity, 0.55297; weight of 1 liter, 0.71549; critical temperature, −82°; critical pressure, 55 atmospheres; boiling-point at a pressure of one atmosphere, −152.5°; freezing-point, −185.8°; specific gravity of liquid methane, 0.415.

According to Bunsen, 1 volume of water absorbs at a temperature t,

$$0.05449 - 0.0011807t + 0.000010278t^2;$$

hence at 20°, 0.0349812 volume.

One volume alcohol absorbs at temperature t,

$$0.522586 - 0.0028655t + 0.0000142t^2;$$

hence at 20°, 0.47096 volume.

$$1 \text{ vol. } CH_4 = 2 \text{ vol. } H + \tfrac{1}{2} \text{ vol. } C,$$

Marsh-gas is always determined by combustion. One volume of methane unites with 2 volumes of oxygen, and 1 volume of carbon dioxide is formed. To avoid the burning of nitrogen in the explosion, 100 volumes of incombustible gas are taken for from 25 to 37 volumes of the mixture of methane and oxygen (Bunsen).

No absorbent for marsh-gas is known.

ETHYLENE (C_2H_4)

Specific gravity, 0.96744; weight of 1 liter, 1.25178; critical temperature, +10°C.; critical pressure, 51 atmospheres; boiling-point at a pressure of one atmosphere, – 102.65°; specific gravity of liquid ethylene, 0.6095,

$$2 \text{ vol. } C_2H_4 = 4 \text{ vol. } H + 2 \text{ vol. } C.$$

One volume of water absorbs at temperature t,

$$0.25629 - 0.00913631t + 0.000188108t^2;$$

hence at 20°, 0.1488 volume (Bunsen).

One volume of alcohol absorbs at $t°$,

$$3.59498 - 0.057716t + 0.0006812t^2;$$

hence at 20°, 2.7131 volumes (Carius).

Ether absorbs about twice its volume, turpentine oil and petroleum two and a half times their volumes, and olive oil its own volume of ethylene.

Either fuming sulphuric acid or bromine water is used for the absorption.

It is advisable to use sulphuric acid so concentrated that when the temperature is slightly lowered, crystals will appear.

The analytical absorbing power is 8.

The acid is used in a simple pipette which has three bulbs (Fig. 82). The small bulb is filled by the glass-blower with glass beads, which serve to give to the sulphuric acid the largest possible surface. With this arrangement the complete absorption of the heavy hydrocarbons, and of ethylene in particular, is effected by passing the gas into the pipette but once.

In this reaction some sulphur dioxide is usually formed, and, moreover, the vapour of fuming sulphuric acid has a very high tension, so that the gas residue, before being measured, must be freed from the acid vapours in the caustic potash pipette, a single passage of the gas into the pipette being also here sufficient.

To avoid having the rubber connections between the pipette and burette attacked by the fuming sulphuric acid, the apparatus is so put together that the sulphuric acid does not quite fill the capillary of the pipette, and the connecting capillary is allowed to

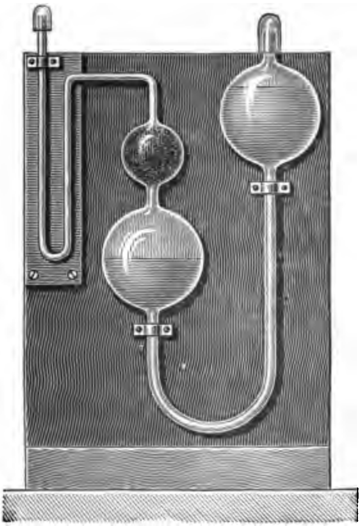
FIG. 82.

remain empty; the short rubber tube of the burette is also freed from liquid by means of a narrow tipped suction pipette, any reagent remaining in the rubber tube being first washed out by water with the same pipette. If care be taken that the sulphuric acid is stopped, after the absorption, at the same point in the capillary at which it stood when the burette and pipette were first put together, then the small volume of air contained in the empty capillary tubes in the beginning causes, of course, no error in the determination of the heavy hydrocarbons or other gases, with the exception of nitrogen. In the nitrogen determination, allowance may be made for this air volume, but as each centimeter of the empty capillary corresponds to only 0.008 ccm., this value falls below the limit of the usual unavoidable experimental errors.

After the absorption, the rubber tube is taken off from the pipette, and the capillary and the larger tube are closed air-tight by little glass caps, which are pushed over narrow rubber rings placed upon the tubes.

Bromine is a good absorbent for ethylene. It is used in a pipette similar to the one just described. It is not necessary to fill the pipette completely with bromine, it being quite sufficient if a few cubic centimeters of bromine lie under water in the pipette. There is thus formed a saturated solution of bromine in water, which absorbs the ethylene. According to experiments of Cl. Winkler,[1] however, the absorption is not a complete one, and it is better to use fuming sulphuric acid for this purpose.

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[1] *Zeitschrift für analyt. Chemie*, **28**, 269–289.

ACETYLENE (C_2H_2)

Specific gravity, 0.89820; weight of 1 liter, 1.16219; critical temperature, 36.9°; critical pressure, 67.96 atmospheres; specific gravity of liquid acetylene at 0° = 0.45.

$$2 \text{ vol. } C_2H_2 = 2 \text{ vol. } H + 2 \text{ vol. } C.$$

Acetylene is somewhat soluble in water,[1] which dissolves its equal volume of the gas. Oil of turpentine and tetra-chlor-methane dissolve 2 volumes of the gas, amyl alcohol and styrol 3½, chloroform and benzol 4, glacial acetic acid and alcohol 6. It is slowly absorbed by concentrated sulphuric acid, acetyl sulphonic acid being formed. An ammoniacal solution of cuprous chloride absorbs the gas rapidly and there is formed a brown to violet-red precipitate of copper-acetylene, which explodes when heated or struck. Acetylene produces in an ammoniacal silver solution a white precipitate similar to the last, but even more explosive than the copper-acetylene. If the gas is led into ammoniacal solutions of aurous thiosulphate, or potassium mercuric iodide, exceptionally explosive compounds are formed.

All of the ammoniacal solutions of metals which have been mentioned may be used as absorbents for acetylene.

Although acetylene can be determined by combustion with oxygen, this method cannot usually be employed, because the gas occurs in mixtures with other combustible gases. One volume of acetylene yields on combustion 2 volumes of carbon dioxide. When 2 volumes of acetylene are burned there is a contraction of 3 volumes.

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[1] The following details are taken from Winkler's *Anleitung zur chemischen Untersuchung der Industrie-Gase*, Part I, p. 109.

$$2\ C_2H_2 + 5\ O_2 = 2\ \underset{\text{liquid}}{H_2O} + 4\ CO_2.$$

It is best determined by leading it through an ammoniacal cuprous chloride solution, a reddish brown precipitate being thrown down. The precipitate is filtered off, and is washed with water containing ammonia until the wash-water passes through colourless.

Since copper-acetylene explodes at 95°, the acetylene is calculated from the copper oxide in the precipitate. The copper-acetylene has the composition[1]

$$C_2Cu_2.$$

To determine the amount of copper present, hydrochloric acid is poured over the copper-acetylene, decomposing it with evolution of acetylene. As it is difficult to completely decompose the copper-acetylene, the end of the reaction is not waited for, but the rest of the precipitate, without being washed, is dried on the filter and ignited. The copper oxide is dissolved in a few drops of nitric acid, and this solution is added to the hydrochloric acid filtrate first obtained. The solution is then precipitated hot with sodium hydroxide, and the copper oxide is filtered off, ignited, and weighed.

The ignition temperature of acetylene when mixed with any more than 35 per cent of air is 480° C. The temperature of dissociation of acetylene is 780° C.

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[1] Keiser, *American Chemical Journal*, 1892, p. 285.

CYANOGEN (C_2N_2)

Specific gravity, 1.79907; weight of 1 liter, 2.32784.

$$2 \text{ vol. } C_2N_2 = 2 \text{ vol. } C + 2 \text{ vol. } N.$$

One volume of water dissolves at 20°, 4.5 volumes of cyanogen; 1 volume of alcohol, 20 volumes of cyanogen.

Burned with twice its volume of oxygen it forms 2 volumes of carbon dioxide and 1 volume of nitrogen.

Cyanogen gas is soluble in benzene.

Free cyanogen, or dicyanogen, may be detected according to Kunz-Krause[1] by the Schönbein-Pagenstecher reaction. For carrying out this test, strips of filter paper are first dipped into a dilute aqueous solution of copper sulphate (1:1000), and are then impregnated with a 3 per cent tincture of gum guaiac. The paper thus prepared turns blue when acted upon by dicyanogen or hydrocyanic acid, but this blue colour is also caused by certain oxidising agents such as ozone and nitric acid.

The reaction is somewhat sharper when the gas mixture, instead of being brought in contact with the paper above described, is passed through a wash-bottle containing an alcoholic copper sulphate — gum guaiac solution.

The reaction has lately been increased in delicacy by E. Schaer, who uses guaiaconic acid in place of the gum guaiac. The reagent should always be freshly prepared, and this is done by adding to 10 ccm. of a dilute aqueous copper sulphate solution

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[1] *Zeitschr. angew. Chem.*, **26** (1901), 652.

15 ccm. of alcohol in which a little guaiaconic acid has previously been dissolved.

Another delicate reaction for dicyanogen is given by Kunz-Krause in the article above cited, this test depending upon the formation of isopurpuric acid or picrocyaminic acid, $C_8H_5N_5O_6$, from picric acid. 2 ccm. of a cold saturated aqueous solution of picric acid (1.86) is mixed with 18 ccm. of alcohol and 5 ccm. of a 15 per cent aqueous solution of potassium hydroxide. When brought into contact with this solution pure cyanogen yields a deep purple red colour, which later turns to brown. On long standing the potassium salt of isopurpuric acid separates in the form of an oil of purple red colour. This reagent also must always be freshly prepared.

Caustic potash absorbs cyanogen, potassium cyanide and potassium cyanate being formed,

$$C_2N_2 + 2\,KOH = KCN + KCNO + H_2O.$$

Cyanogen is determined by absorbing it in a solution of potassium hydroxide, adding silver nitrate, and then slightly acidifying with nitric acid. The precipitate is filtered off, converted into metallic silver by ignition in a porcelain crucible, and is then weighed.

Hydrocyanic Acid (HCN)

Specific gravity, 0.9359; weight of 1 liter, 1.2096. The gas is easily soluble in water and in alcohol. Potassium hydroxide absorbs it, potassium cyanide being formed.

Strong acids, especially hydrochloric acid and sulphuric acid, decompose hydrocyanic acid with formation of formic acid and ammonia.

To detect the acid,[1] add ferrous sulphate and one drop of ferric chloride to the solution of hydrocyanic acid or potassium cyanide, then add potassium hydroxide to alkaline reaction if the solution is not already alkaline, warm gently, and acidify with hydrochloric acid. A dark blue precipitate of Prussian blue results.

Another test for hydrocyanic acid is to add ammonium sulphide until the solution takes on a yellow colour, then ammonia, — or, better, a drop of sodium hydroxide, — and to heat the solution until the excess of ammonium sulphide has been driven off, and the solution is again colourless. In this way there is formed either ammonium or sodium sulphocyanate, which, after acidifying, gives the characteristic blood-red colour with ferric chloride.

Hydrocyanic acid is determined by absorbing it with a solution of potassium hydroxide, and precipitating it with silver nitrate, exactly as given for cyanogen.

The reactions are as follows: —

$$\begin{aligned} HCN + KOH &= KCN + H_2O \\ KCN + AgNO_3 &= AgCN + KNO_3 \end{aligned}$$

HYDROGEN SULPHIDE (H_2S)

Specific gravity, 1.17697; weight of 1 liter, 1.52290; boiling-point, 81.8°; melting-point, – 85°.

$$2 \text{ vol. } H_2S = 2 \text{ vol. } H + 1 \text{ vol. } S.$$

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[1] Cl. Winkler, *Anleitung zur chemischen Untersuchung der Industrie-Gase*, Part I, p. 60.

According to Bunsen's experiments, water absorbs —

At	2° C.,	4.2373 vol.	H_2S
"	9.8° C.,	3.5446 "	H_2S
"	14.6° C.,	3.2651 "	H_2S
"	19° C.,	2.9050 "	H_2S.

Between 2° and 43.3° the absorption by 1 volume water at t°

$$= 4.3706 - 0.083687\,t + 0.0005213\,t^2 \text{ volumes of } H_2S.$$

According to the same authority alcohol takes up, between 1° and 22°, at temperature t,

$$17.891 - 0.65598t + 0.00661t^2 \text{ volumes.}$$

One and a half volumes of oxygen are necessary for the combustion of 1 volume of hydrogen sulphide, and 1 volume of sulphur dioxide is formed.

When sulphur trioxide is brought into contact with hydrogen sulphide, sulphuric acid, sulphur dioxide, and sulphur result —

$$2\,SO_3 + H_2S = H_2SO_4 + SO_2 + S.$$

Potassium hydroxide and solutions of many of the heavier metals absorb hydrogen sulphide, and give the corresponding compound.[1]

If hydrogen sulphide is present in any considerable amount, its presence is shown by its odour. A surer test is to introduce into the gas a strip of so-called lead-paper. The paper becomes covered with a glistening brownish black layer of lead sulphide, even when only traces of hydrogen sulphide are present.

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part I, p. 60.

Concentrated nitric acid and solutions of chromic acid, permanganic acid, ferric oxide, chlorine, bromine, iodine, and of the oxygen acids of the last three, decompose hydrogen sulphide immediately, with the separation of free sulphur; in the presence of an excess of the halogens, the sulphur is finally attacked and wholly or partly converted into sulphuric acid.

Hydrogen sulphide may be quantitatively determined by Dupasquier's method, a measured quantity of gas (see Fig. 62) being drawn through a solution of iodine in potassium iodide, to which some starch paste has been added. The operation is stopped as soon as the solution becomes colourless. The reaction is —

$$H_2S + I_2 = 2HI + S,$$

but the reaction follows this equation precisely only when the solutions are very dilute and protected from direct sunlight.

R. Fresenius[1] determines hydrogen sulphide gravimetrically by first drying the gases with calcium chloride and then absorbing the hydrogen sulphide in U-tubes which are filled $\frac{5}{6}$ with pumice-stone impregnated with copper sulphate, and $\frac{1}{6}$, at the exit end, with calcium chloride. The pumice-stone is prepared as follows: Place 60 g. of pumice-stone, in pieces the size of a pea, in a small porcelain dish, and pour a hot concentrated solution of from 30 to 35 g. of copper sulphate over it. Evaporate the solution to dryness with constant stirring, place the dish in an air- or oil-bath, whose temperature is kept between 150° and 160° C., and let it remain there four hours.

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[1] R. Fresenius, *Anleitung zur quant. Analyse*, 6th ed., Part I, p. 505. Also *Zeitschr. f. analyt. Chemie*, **10**, 75.

A tube containing 14 g. of this copper sulphate pumice-stone takes up about 2 g. of hydrogen sulphide. To make sure of complete absorption two such tubes should always be used. When the pumice-stone is less thoroughly dried, it takes up a much smaller amount of hydrogen sulphide, and when it has been dried at a higher heat — until it has lost its water of crystallisation — it causes a decomposition of the hydrogen sulphide and the evolution of sulphur dioxide.

Hydrogen sulphide can also be determined by passing the gas through a solution of bromine in water, precipitating the sulphuric acid thus formed with barium chloride, and weighing as barium sulphate.

According to Bunsen[1] it is possible to determine the hydrogen sulphide of a gas mixture containing hydrogen, nitrogen, carbon dioxide, hydrocarbons, etc., by means of balls of manganese dioxide. The purest pyrolusite is ground to a very fine powder, and is then stirred with sufficient distilled water to make a thin paste. The balls are made from this paste by pressing it in a bullet-mould which has been rubbed with oil. The balls are dried in an air-bath, and are then covered with a concentrated sirupy solution of phosphoric acid.

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[1] Bunsen, *Gasometrische Methoden*, 2d ed., p. 111.

SULPHUR DIOXIDE (SO_2)

Specific gravity, 2.21295; weight of 1 liter, 2.86336; melting-point, −76°; boiling-point, −8°; specific gravity of liquid sulphur dioxide at −20° = 1.49.

$$2 \text{ vol. } SO_2 = 1 \text{ vol. } S + 2 \text{ vol. } O.$$

Sulphur dioxide is easily soluble in water. According to Sims, 1 volume of water dissolves at 760 mm. pressure —

At 7°,	61.65	vol.	SO_2
" 20°,	36.43	"	SO_2
" 39.8°,	20.5	"	SO_2
" 50°,	15.62	"	SO_2.

One volume of water absorbs at 76 cm. pressure, and at temperatures between 0° and 20°, at $t°$,

$$79.789 - 2.6077t + 0.029349\,t^2$$

volumes of sulphur dioxide; hence, 1 volume of the saturated aqueous solution contains, at $t°$,

$$68.861 - 1.87025\,t + 0.01225\,t^2$$

volumes of the gaseous acid.

For temperatures between 21° and 40°, the coefficient of absorption is —

$$75.182 - 2.1716\,t + 0.01903\,t^2,$$

and the amount of gas contained by the saturated aqueous solution is —

$$60.952 - 1.38898\,t + 0.00726\,t^2 \text{ volumes.}$$

In the solution which has been saturated at 0°, a hydrate separates out in crystals. These crystals melt between 1° and 2° with evolution of gas, and probably have the formula —

$$H_2SO_3 + 14\,H_2O.$$

The solution of the gas has a strong acid reaction, and reddens blue litmus paper. This the completely dry gas does not do, because sulphurous acid, H_2SO_3, is formed only when the gas unites with water.

The gas is condensed by pressure or cold to a colourless mobile liquid which boils at $-8°$.

One volume of alcohol absorbs at 760 mm. pressure and $t°$, $328.62 - 16.95\,t + 0.3119\,t^2$ volumes of sulphur dioxide. The specific gravity of the solution is then —

$$1.11937 - 0.014091\,t + 0.000257\,t^2 \text{ (Carius).}$$

The alcoholic solution of sulphur dioxide, saturated at 0°, contains 216.4 volumes of the gas.

Alkalies absorbed the gas very actively, with evolution of heat.

Sulphur dioxide is determined either by leading a measured volume of the gas through a solution of bromine in water, and precipitating the sulphuric acid thus formed by barium chloride, or by measuring the amount of gas required to decolourise an iodine solution of known strength.

In the latter method the reaction, when it takes place in aqueous solutions, follows this equation,

$$SO_2 + I_2 + 2\,H_2O = H_2SO_4 + 2\,HI,$$

so long as the liquid does not contain more than 0.04 per cent of sulphur dioxide (Bunsen).

Reich has applied this method to the determining of sulphur dioxide in the gases from roasting furnaces (see p. 323).

$$1 \text{ ccm. } \frac{N}{10} \text{ iodine solution} = 0.0032 \text{ g.} = 0.11 \text{ ccm. } SO_2.$$

CARBON OXYSULPHIDE (COS)

Specific gravity, 2.07483; weight of 1 liter, 2.68464.

Experimentation with carbon oxysulphide is especially difficult because the gas is easily decomposed by contact with water, alkalies, and acids, especially in the light.

Pure carbon oxysulphide has a very slight odour and is very poisonous.

The critical temperature is 105° C.; critical pressure, 63 kg. per square centimeter; boiling-point at atmospheric pressure, $-47.5°$ C. The pressure of the gas at 17.4° C. is 8 kg. per square centimeter. 1 ccm. of water at 13.5° and 756 mm. pressure absorbs 0.8 ccm. of carbon oxysulphide. The analytical absorbing power of a solution, prepared by dissolving one part of potassium hydroxide in two parts of water and adding an equal volume of alcohol, is 18; that is, a cubic centimeter of this reagent is able to absorb 72 ccm. of carbon oxysulphide. The gas is but slightly soluble in a hydrochloric acid solution of cuprous chloride. 1 ccm. of this solution absorbs about 0.2 ccm. of the gas.

$$2 \text{ vol. } COS = 1 \text{ vol. } C + 1 \text{ vol. } O + 1 \text{ vol. } S.$$

Water absorbs about its own volume of the gas, and takes on its odour and sweet, sharp taste. The gas is probably present in many sulphur springs.

One volume of carbon oxysulphide needs 1½ volumes of oxygen for its combustion, and yields 1 volume of CO_2 and 1 volume of SO_2. The mixture explodes with a loud sound and a brilliant white flame. With 7½ volumes of air it burns quietly.[1]

In a mixture of air and carbon oxysulphide, the latter can be quantitatively determined by combustion even when the work is carried on over aqueous solutions. The total contraction resulting from the combustion of the gas and the subsequent absorption by potassium hydroxide of the sulphur dioxide and carbon dioxide that are formed is measured, and 2½ times this contraction gives the volume of carbon oxysulphide which was present.

When mixed with hydrogen sulphide and carbon dioxide, carbon oxysulphide may be determined by first absorbing the hydrogen sulphide with an acid solution of copper sulphate (see table below), then decomposing the carbon oxysulphide by heat into carbon monoxide and sulphur, absorbing the carbon monoxide with a hydrochloric acid solution of cuprous chloride, and finally determining the carbon dioxide which may be present by means of potassium hydroxide.

The heating of the carbon oxysulphide is carried on in a platinum capillary. Care must be exercised to see that the ends of the capillary are not stopped up by solidifying sulphur. If this should occur, the sulphur can be melted by heating the capillary up to 120°. The volume of the carbon monoxide which is found corresponds exactly to that of the carbon oxysulphide. Inasmuch as carbon oxysulphide is not absorbed by a hydrochloric acid solution of cuprous chloride, it can be separated from carbon monoxide by means of this reagent.

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part I, p. 111.

The great solubility of all of the gases present in such a mixture as that described just above, and the instability of the carbon oxysulphide itself, make it impossible to obtain results of any high degree of accuracy. An artificially prepared mixture, consisting of

44.3	per cent,	COS
37.6	"	H_2S
14.2	"	CO_2
3.9	"	$N + O + H$,

gave upon analysis the following results: 62.2 ccm. of the mixture treated with 15 ccm. of an acid copper sulphate solution showed an absorption of 22.4 ccm. of H_2S, equal to 36 per cent of that gas. The remainder of the gas was heated and a diminution in volume amounting to 39.1 ccm. resulted. After absorption with hydrochloric acid cuprous chloride, 13.5 ccm remained, the difference, 26.3 ccm. (=42.3 per cent), representing the COS present. After absorption with potassium hydroxide, 5.5 ccm. of gas remained, showing 8 ccm., or 12 per cent, of CO_2 present in the mixture.

These values show that the results which are obtained by separating these gases by absorption are only approximate.

Reagent Employed	Analytical Absorbing Power		
	Carbon Oxysulphide	Hydrogen Sulphide	Carbon Bisulphide
Chloroform	—	—	2–3
Mixture { 1 part triethylphosphine 9 parts chloroform	—	—	16
Pyridine	1.1	4–5	9
Mixture { 1 part triethylphosphine 9 parts pyridine 10 parts nitrobenzene	3	26	26
Nitrobenzene	3	2	46
1 part potassium hydroxide in 2 parts water. One-half saturated with H_2S, and the 2 portions then mixed	—	—	1
Saturated solution of copper sulphate in a mixture of 200 gr. water and 200 gr. concentrated sulphuric acid	—	2.2	—

If carbon oxysulphide is led through heated alkaline earths, alkalies, or a layer of red-hot soda lime, it is wholly absorbed—

$$COS + 2\,CaO = CaS + CaCO_3.$$

Chlorine (Cl)

Specific gravity, 2.44921; weight of 1 liter, 3.16906; critical temperature, + 141°; critical pressure 83.3

atmospheres; boiling-point at a pressure of one atmosphere – 33.6°; specific gravity of liquid chlorine = 1.557.

Chlorine is quite soluble in water. One part of cold water dissolves approximately 2 volumes of chlorine; hot water dissolves less. Experiments by Roscoe have shown that the absorptions do not follow the usual laws of absorption. According to Schönfeld, 1 volume of water absorbs the following volumes of chlorine: —

10°,	2.5852
15°,	2.3681
20°,	2.1565
25°,	1.9504
30°,	1.7499
35°,	1.5550
40°,	1.3656.

Chlorine is best determined by the Bunsen procedure, in which the gas is led through a solution of potassium iodide, and the iodine set free is titrated with sodium thiosulphate —

$$Cl_2 + 2\,KI = 2\,KCl + I_2,$$
$$2\,Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\,NaI.$$

Chlorine can also be absorbed with potassium hydroxide or caustic soda. In cold dilute solutions potassium hypochlorite is formed —

$$2\,KOH + Cl_2 = KClO + KCl + H_2O.$$

In hot concentrated solutions, the reaction is —

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

According to R. v. Wagner, the hypochlorite formed may, after addition of potassium iodide and hydrochloric acid, be titrated with sodium thiosulphate.

If a solution contains free chlorine together with hydrochloric acid, they may both be determined in the following manner (Fresenius): —

To a weighed portion of the liquid add an aqueous solution of sulphurous acid until the latter is in excess; after some time add nitric acid and then some potassium chromate to destroy the excess of sulphur dioxide, and precipitate the total chlorine as silver chloride.

If now the amount of free chlorine is determined in a second portion by potassium iodide, the difference gives the quantity of chlorine present in the form of chloride.

The total chlorine may also be volumetrically determined by absorbing the gases with a solution of sodium hydroxide, adding sulphur dioxide, then, after a while, nitric acid and some potassium chromate, and finally neutralising the solution by adding calcium carbonate. All chlorine is now present as chloride, and the solution is neutral, so that the chlorine may be titrated with a neutral silver solution, potassium chromate being used as indicator.

HYDROCHLORIC ACID (HCl)

Specific gravity, 1.25922; weight of 1 liter, 1.62932; boiling-point, −80.3°; melting-point, −112.5°; specific gravity of liquid hydrochloric acid, 1.27.

$$2 \text{ vol. HCl} = 1 \text{ vol. Cl} + 1 \text{ vol. H.}$$

Hydrochloric acid dissolves very easily in water, in ice, and in salts containing water of crystallisation, as Glauber's salt, copper sulphate, magnesium sulphate, borax, etc.

According to Roscoe and Dittmar, 1 volume of water dissolves at 0°, 503 volumes of the gas. The parts by weight of the gas which dissolve in 1 g. of water at a pressure of 760 mm. and at different temperatures, are given in the following table : —

Temperature	HCl	Temperature	HCl
0	0.825	32	0.665
4	0.804	36	0.649
8	0.783	40	0.633
12	0.762	44	0.618
16	0.742	48	0.603
20	0.721	52	0.589
24	0.700	56	0.575
28	0.682	60	0.561

At ordinary temperatures, 1 volume of alcohol dissolves 327 volumes of hydrochloric acid.

At a pressure of from 30 to 40 atmospheres, the gas condenses to a colourless liquid of strong refractive power.

If no other acid gas is present with the hydrochloric acid, it can be determined by drawing a measured quantity of the gas through a standardised solution of an alkali and titrating back with an acid.

Hydrochloric acid may be accurately determined by absorbing it with an alkaline solution free from chlorine, and, after acidifying, precipitating it with silver nitrate, and weighing as silver chloride.

A method proposed by Cl. Winkler,[1] and based upon J. Volhard's volumetric method for the determination of silver,[1] consists in placing in a suitable absorption apparatus a few drops of ammonium sulphocyanate or potassium sulphocyanate, some iron alum solution, and a measured amount of $\frac{N}{10}$ silver nitrate solution. Upon leading the gas through this solution the hydrochloric acid unites with the silver, forming silver chloride. The end of the reaction is shown by the blood-red colour. The cause of this colour is, that after all of the silver nitrate has been changed to silver chloride, the silver sulphocyanate present is also decomposed and ferric sulphocyanate is formed. The volume of the gas is measured and the amount of hydrochloric acid it contains is calculated.

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II, p. 322.

SILICON TETRAFLUORIDE (SiF_4)

Specific gravity, 3.60469; weight of 1 liter, 4.66414.

$$2 \text{ vol. } SiF_4 = 1 \text{ vol. } Si + 4 \text{ vol. } F.$$

The gas is completely taken up by water, being at the same time decomposed —

$$3\, SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6.$$

This reaction, which has been employed by R. Fresenius[2] for the quantitative determination of fluorine, might possibly be made use of for the determination of silicon tetrafluoride in gases; up to the present time, however, no satisfactory method has been devised. The silicon tetrafluoride probably formed in fusion processes is always mixed with large amounts of steam, dust, and sulphur dioxide, and for these reasons its determination is exceptionally difficult.

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[1] J. Volhard, *Zeitschrift für analyt. Chemie*, **13**, 171, and **17**, 482.

[2] Fresenius, *Quant. chemische Analyse*, 6th ed., Part I, p. 431.

PHOSPHINE (PH_3)

Specific gravity, 1.17552; weight of 1 liter, 1.52102.

$$2 \text{ vol. } PH_3 = \tfrac{1}{2} \text{ vol. } P + 3 \text{ vol. } H.$$

Phosphine is a colourless gas with a very unpleasant odour, resembling that of decayed fish. It is very poisonous. The pure gas takes fire only at a temperature above 100°, but the friction of the stopper of the bottle containing the gas is often sufficient to ignite it.

It can be mixed with pure oxygen without change, but if the mixture be suddenly brought under diminished pressure, it explodes. Phosphine takes fire when brought in contact with a drop of fuming nitric acid, or with the vapour of chlorine or bromine.

Phosphine is somewhat soluble in water. One volume of water absorbs about 0.02 volume of the gas, and takes on its odour and disgusting taste. Exposed to the light, the solution decomposes with evolution of hydrogen and separation of amorphous phosphorus. The gas is decomposed by electric sparks into phosphorus and hydrogen, the resulting volume being exactly $1\frac{1}{2}$ times that at the beginning.

Phosphine combines, as does ammonia, with metallic chlorides, aluminium chloride, tin chloride, and antimony chloride.

The gas cannot be detected by means of lead-paper, but strips of paper impregnated with silver nitrate are turned black at once, metallic silver separating out and phosphoric acid being formed.

Phosphine can be determined by drawing the gas in question through bromine water and then precipitating the resulting phosphoric acid by magnesia mixture. If a silver solution has been used for the absorption, the excess of silver must first be removed by hydrochloric acid.

The phosphoric acid thus formed may also be detected with ammonium molybdate.

According to J. Riban[1] a hydrochloric acid solution of cuprous chloride absorbs phosphine.

The best absorbent for determining phosphine in the presence of acetylene is a solution of copper sulphate containing free sulphuric acid.[2] (See p. 316.)

ARSINE (AsH_3)

Specific gravity, 2.69728; weight of 1 liter, 3.49003.

$$2 \text{ vol. } AsH_3 = \tfrac{1}{2} \text{ vol. } As + 3 \text{ vol. } H.$$

Arsine is a colourless gas of very unpleasant odour. It burns with a blue flame, with formation of white clouds of arsenic trioxide. When passed through a highly heated tube, the gas is decomposed and a glistening mirror of metallic arsenic is deposited.

When arsine is led over red-hot copper oxide, water and copper arsenide are formed. Arsine may be easily detected in this manner. If arsine is passed over heated metals, such as tin, potassium, or sodium, arsenides are formed and hydrogen is set free.

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[1] *Compt. rend.*, **88**, 581.

[2] Hempel and Kahl, *Zeitschr. f. angew. Chemie*, 1898, p. 53.

Arsine precipitates the metal from solutions of gold and silver salts —

$$AsH_3 + 6AgNO_3 + 3H_2O = As(OH)_3 + 6HNO_3 + 6Ag,$$

and if an aqueous solution of ammonia be carefully added to the filtrate, a yellow ring of silver arsenite is formed. Minute quantities of arsenic may be detected in this manner.

Water absorbs five times its volume of arsine.

Bromine, chlorine, and iodine decompose the gas.

A very suitable method for the determination of arsine consists in leading it into a silver solution, precipitating the excess of silver by hydrochloric acid, filtering, and, after warming, precipitating the arsenic with magnesia mixture. The precipitate is ignited and weighed as $Mg_2As_2O_7$.

Arsine can be completely removed from hydrogen sulphide by leading the mixture of the two gases through a tube which contains pieces of iodine.

STIBINE (SbH_3)

Specific gravity, 4.3287; weight of 1 liter, 5.6.

$$2 \text{ vol. } SbH_3 = \tfrac{1}{2} \text{ vol. } Sb + 3 \text{ vol. } H.$$

Water absorbs from 4 to 5 volumes of the gas at 10°. Stibine burns with a greenish flame, and gives off white fumes of antimony trioxide.

If the gas be led through glass tubes heated to redness, metallic antimony is deposited in the form of a mirror a short distance beyond the heated point.

If stibine be passed into a solution of silver nitrate, black silver antimonide, $SbAg_3$, mixed with metallic silver, is precipitated.

Sulphur, when exposed to the light, or when heated to above 100°, decomposes the gas and becomes coated with orange-red antimony sulphide —

$$2\ SbH_3 + 6\ S = Sb_2S_3 + 3\ H_2S.$$

Hydrogen sulphide acts similarly in the light —

$$2\ SbH_3 + 3\ H_2S = Sb_2S_3 + 6\ H_2.$$

Concentrated nitric acid and potassium permanganate oxidise the gas. Stibine does not blacken lead-paper.

Stibine may be determined by leading the gas under examination into a silver solution, filtering off the silver antimonide formed, and digesting it with ammonium sulphide. The antimony goes into solution as ammonium sulphantimonite, and after being thrown down again, it can be weighed as antimony sulphide, or it may be converted into antimony tetroxide and weighed as such.

PART III

PRACTICAL APPLICATIONS OF GAS ANALYSIS

CHAPTER I

COMBUSTION GASES—FURNACE GASES

In many industries the profits are largely dependent upon the amounts paid out for fuel, so that in all factories having large furnaces a systematic examination of the working of the furnace is of considerable importance. The driving of a fire is the more favourable the less the excess of air beyond the amount necessary for producing complete combustion. In many boiler plants which seem to be otherwise well constructed, the examination shows that an enormous excess of air is being used, and that a correspondingly large amount of heat is being allowed to pass unused into the chimney. It is impracticable to wholly abstract the heat from the gases from the fire; a certain amount of heat must be left in them, so that they will move rapidly enough in the chimney. It follows that a disproportionately large amount of heat will be lost when the draught in the furnace is too strong. Even the most skilful stoker will not be able to tell merely from the appearance of the fire exactly how the combustion is proceeding. For these reasons it is advisable to adopt some arrangement which will continually draw off a small current of gas from the fire, and to give the stoker a bonus which is higher the less oxygen there is in the departing gases.

To judge of the combustion, it is quite sufficient to make merely a determination of the oxygen, for the amounts of all other products of combustion are of course dependent upon the oxygen, provided that the furnace is not giving off thick clouds of smoke, *i.e.* that, instead of burning, the fire merely smoulders.

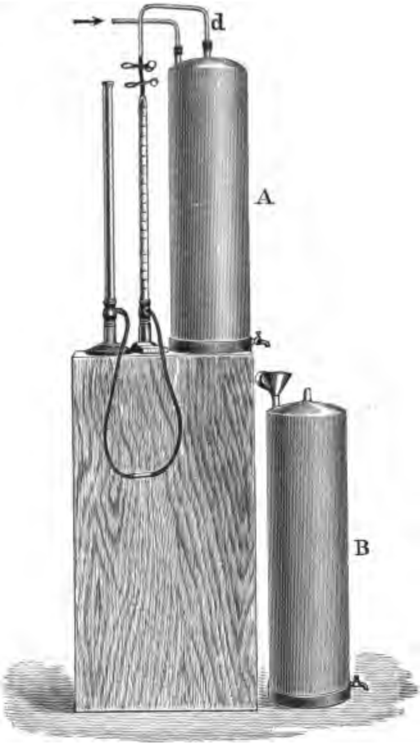

FIG. 83.

The tube for taking off the gases is introduced into the flue at a place which is selected with reference to the points mentioned on p. 3. It is convenient to connect the tube with a bottle aspirator made of ordinary sheet-zinc (see Fig. 83). The water is allowed to drop from *A* into *B*, and its flow can easily be so regulated that the water will flow out of *A* once in six, twelve, or twenty-four hours. The analysis of this gas sample gives the average composition of the furnace gases. The tube *d*, which reaches to about the middle of *A*, serves for taking off samples with the gas burette.

Well-managed furnaces should give not more than about 8 per cent of free oxygen. The furnaces of the present day may be said to be exceptionally good when the gases from the fire contain only from 3 to 4 per cent of oxygen.

If a more complete analysis of the furnace gases is desired, the procedure is exactly the same as that given for the analysis of generator gases.

Furnace gases usually contain only carbon dioxide, oxygen, and nitrogen. All other gases are present in but very small amounts. In oft-repeated analyses the author has always found only traces of carbon monoxide, methane, and the heavy hydro-carbons.

The apparatus necessary for thus controlling the working of a furnace is—

1. A bottle aspirator, with the necessary tubes, for collecting the gas.
2. A simple gas burette.
3. A pipette for solid absorbents, which is filled with phosphorus and kept in a light-tight box.

The analysis of a gas mixture from a furnace may also be made with the Orsat apparatus. Many modifications of this have been devised, but the form shown in Fig. 84, is that most generally used. It consists of the measuring burette *a* containing 100 ccm., and of the absorption bulbs *b*, *c*, and *d*. The burette is joined at the lower end with a level-bulb and at the upper end with a long capillary tube which has three branch tubes, each supplied with a glass stopcock. The absorption bulbs are connected to these branch tubes in the manner shown in the figure and are usually filled with glass tubes which serve to bring the various reagents into intimate contact with the gas mixture. The absorption bulb *b* contains a concentrated solution of potassium hydroxide for the absorption of carbon dioxide. *c* contains an alkaline solution of pyrogallol, while *d* is filled with a hydrochloric acid solution of cuprous chloride. The gas mixture which is to be analysed is drawn into the apparatus through the outer end of the capillary by first opening the stopcock *k*, raising the level-bulb until the burette and the capillary are filled with water, and then lowering the level-bulb, the stopcock *k* being, of course, closed after the gas has been drawn in. Before beginning the operation the reagents in the three absorption bulbs should first be drawn up to marks on the capillary tubes above the bulbs. It is convenient to work with a sample of exactly 100 ccm., this being measured off in the manner described for the Hempel apparatus on p. 37. The gas is then first driven over into *b* to absorb carbon dioxide and is drawn back into the burette and measured. The reagent in the absorption bulb must, of course, be brought to the height at which it first stood. After the carbon dioxide has been thus determined, the gas is passed over into the second absorption bulb and oxygen is removed, and finally the carbon mon~~di~~oxide is absorbed in the third bulb. Some forms of the Orsat apparatus are supplied also with a palladium asbestos tube *f*, for the determination of the combustible gases.

The Orsat apparatus is quite extensively used at the present time, because it is easy to manipulate

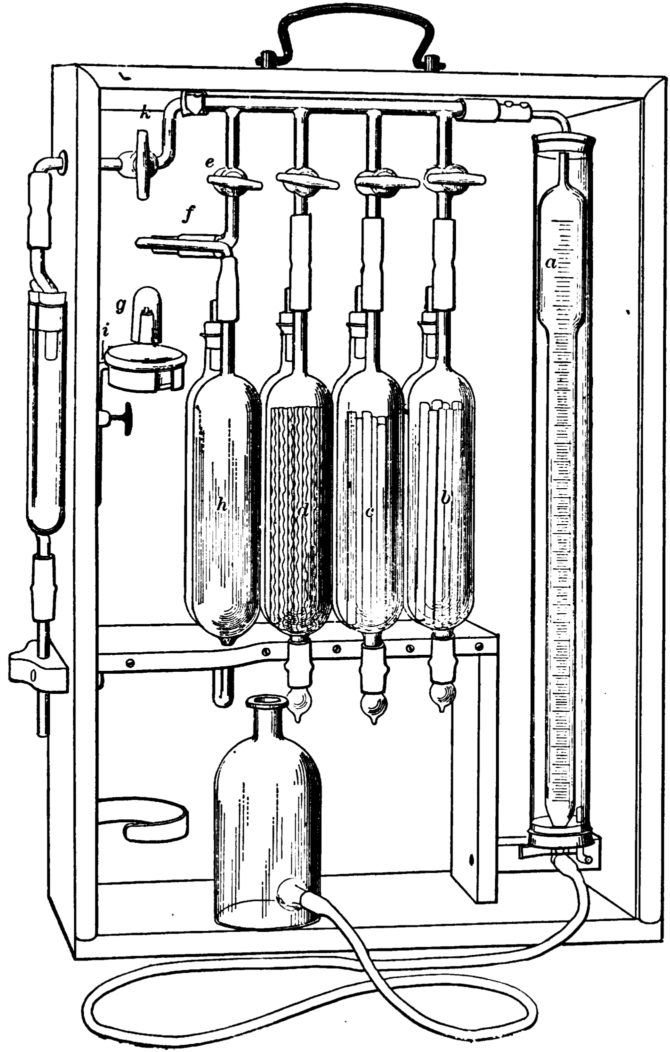
k
e
f
g
i
h
d
c
b
a
o

FIG. 84.

and is so compact that it can conveniently be carried about. It cannot, however, be recommended because, first, the long capillary connection between the burette and the absorption bulb contains a volume of gas sufficient to seriously influence the accuracy of the work; second, the long capillary tube with its branch tubes and glass stopcocks is fragile and costly, and if it is broken it can be repaired only by an expert-glass blower; third, the reagents in the second and third absorption bulbs are not fully protected from the action of the air and consequently deteriorate rapidly (some manufacturers attach thin rubber bulbs to the open end of the absorption bulb to protect the reagent from the air, but these rubber bulbs are most unsatisfactory); and fourth, and most important of all, the apparatus does not permit of the reagent in the second and third bulb being shaken with the gas mixture, the result being that the absorption of oxygen and carbon monoxide takes place very slowly and is rarely complete. A comparison of various methods for determining carbon monoxide[1] gave the following results for the Orsat apparatus: —

Gas mixture contained	Average of Six Determinations with the Orsat Apparatus
3 per cent carbon monoxide	2.31 per cent
9 " " "	8.50 "
15 " " "	14.40 "

An idea of the completeness of the combustion in a heating plant may be obtained in a moment without the aid of a chemical examination by using an apparatus which shows the specific gravity of the escaping gases. The gases in question are continuously drawn through the apparatus by means of a

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[1] Dennis and Edgar, *J. Am. Chem. Soc.*, **19**, 859.

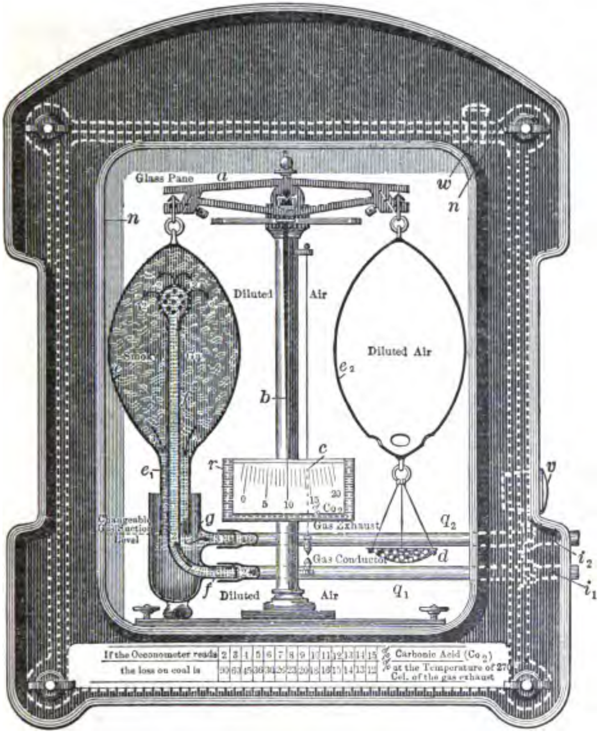
Glass Pane
a
w
n
n
Diluted
Air
Smoke
Diluted Air
e_2
b
c
r
e_1
0
5
10
15
20
% CO_2
Changeable Gas Suction Level
g
Gas Exhaust
q_2
Gas Conductor
d
f
Diluted
Air
q_1
v
i_2
i_1
If the Oeconometer reads
2 3 4 5 6 7 8 9 10 11 12 13 14 15
% Carbonic Acid (CO_2)
the loss on coal is
90 63 45 36 30 25 23 20 18 16 15 14 13 12
% at the Temperature of 270 Cel. of the gas exhaust

FIG. 85.

steam or water suction pump, but before entering they must pass through a cotton filter to remove flue dust and soot, and must be freed from moisture by means of calcium chloride.

The apparatus for determining the specific gravity of gases in this manner is termed a gas balance. A number of different forms have been devised. In addition to the one to be described on p. 273, Fig. 89, which was devised by Lux, the gas balance original with Arndt has been found to be quite satisfactory (Fig. 85). This consists essentially of a fine balance, carrying on one end of the beam a closed glass vessel, pan, and weights, while to the other beam end is attached an open glass vessel (shaded in the figure) through which passes the gas mixture which is being examined, the gas entering through tube 2 and passing out through tube 3.

Such balances will not, of course, correctly show the presence of unburned gases.

With normal working of the heating plant these gas balances are convenient and fairly accurate; but if variations from the normal occur in the firing, they do not give satisfactory results.

CHAPTER II

ILLUMINATING GAS

WATER GAS — GENERATOR GAS — BLAST-FURNACE GASES — COKE-FURNACE GASES

THE gases formed in dry distillation of coal are quantitatively of very different composition. All of them contain hydrocarbon vapours, carbon dioxide, carbon monoxide, heavy hydrocarbons, marsh-gas, hydrogen, water, and nitrogen, and most of them contain also some oxygen which has entered through leakages in the apparatus.

The unpurified gas contains hydrogen sulphide, ammonia, uncondensed tar, as well as carbon disulphide and organic sulphur compounds.

In the examination of illuminating gas there must be made —

1. A photometric measurement of the illuminating power of the gas.
2. The determination of the specific gravity of the gas.
3. The determination of tar and the constituents separable by cooling.
4. The volumetric analysis of the gaseous constituents.

5. The determination of sulphur.
6. The determination of ammonia.
7. The determination of carbon dioxide.

1. *The Measurement of the Illuminating Power*

The amount of light generated by an illuminating gas in burning is dependent upon the construction of the burner, so that this determination is accompanied by large errors.

Up to the present time there exists no perfectly accurate and simple method for determining the illuminating power of a flame. When we remember that the light given out by ordinary lamps is composed of a great number of rays of different colours which result from their different wave-lengths, and which cannot be directly compared with one another, it is easy to understand that the results of the determinations are, under certain conditions, quite variable.

If candle flames and gas flames are compared, the photometric measurements agree quite satisfactorily. If, however, the yellow light of a candle be compared with the white light of a Siemens regenerative burner, an electric lamp, or an Auer von Welsbach incandescent light, one will find it quite impossible to make even approximately accurate measurements, and the uncertainty in the determination will amount to more than a whole candle power. The explanation of this is, that while similarly coloured sources of light may be directly measured in the photometer, lights of different colours cannot be compared with one another. The electric light, which is rich in blue rays, cannot be compared with a candle flame, which possesses but few of these rays. The coloured rays are not of equal value for purposes of illumination, and a correct idea of the lighting power of any appliance can be obtained only by breaking up the light by means of a spectro-photometer, and then ascertaining how much of each sort of light is present. Several spectro-photometers for purely scientific researches have been devised.

For controlling the working of gasworks, the measurement of illuminating power is nevertheless of great value, because it can be quickly made. But it should not be forgotten that only gases of similar composition can be compared with one another. If one wished to compare oil-gas with ordinary illuminating gas, he would immediately be confronted by the difficulty that there is no burner in which both gases can be burned with equal advantage. For this reason the kind of burner in which the gas was burned should be exactly stated in all photometric measurements.

For ordinary illuminating gas the so-called normal burner of Elsler has been adopted in Germany. This is an Argand burner consuming 150 liters per hour, and which must show, when burning, a pressure of 2.5 mm. in the burner.

The unit of light in use in Germany is a candle of paraffin with melting-point 55° C. The candle has a diameter of 20 mm., and six of them weigh 500 g. The wick, which weighs 0.668 g. per meter, consists of twenty-four cotton threads, one of which is red so that the candles may be easily distinguished. The height of the flame is 50 mm.

Instead of this candle an amyl acetate lamp of the Hafner-Alteneck construction is sometimes used. An advantage possessed by the amyl acetate lamp is, that when once it has been regulated it burns without change for a long time, while, with a candle, the height of the flame must be constantly regulated by cutting off the wick. 1000 of the above candles are equal to 977 of the English spermaceti candles, and to 102 Paris Carcel-lamps.

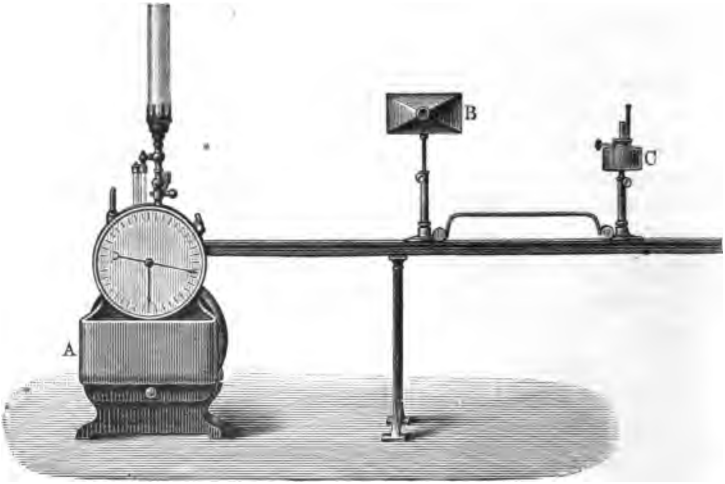

FIG. 86.

The measurement of the illuminating power may be made with a Bunsen photometer (Fig. 86). This consists of a partly translucent screen of paper, which can be moved back and forth between the normal light and the flame under examination. In measuring, the screen is brought into such a position that the translucent spot appears equally dark on both sides, the observation being easily made by means of two mirrors in *B*, placed at the proper angles.

In this position the screen is illuminated with equal intensity by the two sources of light. The ratio between the illuminating power of the flame that is being tested and that of the normal flame, is as the squares of the distances of the flames from the screen.

The photometer is usually so arranged that the normal flame is fastened, at a definite distance from the screen, to a slide which moves along a track. On this track is a scale, from which the illuminating power may be directly read off.

The paper screen is best made from fine white drawing-paper that does not glisten, and that is about as thick as ordinary writing-paper. A cork is dipped into molten paraffin, stearin, or spermaceti, and is then pressed upon the middle of the paper. When the fat has cooled it is scraped off with a knife, and the paper is warmed until the spot appears uniformly translucent. If it is too nearly transparent, the paper is laid between two sheets of clean blotting-paper and pressed with a warm flat-iron.

The photometer has been improved,[1] the fat spot being replaced by an optical arrangement consisting essentially of two prisms, by means of which the light from one source appears as a spot surrounded by the light from the other source. In this way a very sharp comparison of the illuminating powers of the two flames is made possible.

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[1] O. Lummer and E. Brodhun, "Ersatz des Photometerfettflecks durch eine rein optische Vorrichtung," *Zeitschrift für Instrumentenkunde*, 1889, pp. 23 and 41.

To determine the candle power of an illuminating gas, the consumption of the flame is first brought to 150 liters per hour by means of an experimental gas-meter. The flame of the normal candle or amyl acetate lamp having been brought to the proper height, the photometric measurement is made.

The measurement should be made in a room with blackened walls, and with windows which can be covered light-tight by black curtains. The room itself should be dry and well ventilated, since the accumulation of carbon dioxide changes considerably the illuminating power of a flame. The gas passing to the normal burner must never be led through long pieces of rubber tubing, because they would change its illuminating power.

Unless the gas-meter is in constant use, the gas must burn in the normal burner for at least two hours before the measurement is made.[1]

2. *The Determination of the Specific Gravity*

The determination of the specific gravity is most conveniently made by Bunsen's method[2] of measuring the speed of escape of the gas.

This method is based upon the fact that the specific gravities of two gases escaping through narrow openings in thin plates bear nearly the same ratio to each other as the squares of their speeds of escape. If a gas of the specific gravity s has a speed of flow t, and another gas of a specific gravity s_1 has a speed of flow t_1, the relation between the speed of escape and the specific gravity is given by the equation —

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[1] Given in detail in N. H. Schilling's *Handbuch für Steinkohlengas-Beleuchtung.*

[2] Bunsen, *Gasometrische Methoden*, 2d ed., p. 184.

$$\frac{s_1}{s} = \frac{t_1^2}{t^2}.$$

If s or the specific gravity of one of the gases be regarded as 1, the specific gravity of the other gas is found by the formula —

$$s_1 = \frac{t_1^2}{t^2}.$$

Figure 87 shows the apparatus used for this determination. A glass tube of about 70 ccm. capacity is luted into the iron cap *A*. This cap is fitted with a three-way stopcock by means of which the inside of the glass tube can be brought into communication with either the tube *B*, through which the gases are introduced, or the small opening in *C*. This opening is made in a platinum plate, which is about as thick as tin foil, and is luted in position. To obtain a platinum plate as thin and an opening as small as possible, the platinum foil is pierced with a fine sewing needle, and is hammered with a polished hammer upon a polished anvil until the opening can no longer be seen with the naked eye, and is only visible when the plate is held between the eye and a bright flame. The plate thus perforated is cut out in the form of a small circular disk, the opening being at the centre.

In order that the gases to be examined may always escape through the opening *C* under the same conditions as regards pressure, there is placed in *A* a float *bb*. This float should be as light as possible, and for this reason it is best made from a very thin-walled glass tube. The float has at β a little button of black glass from which projects a small, white glass point.

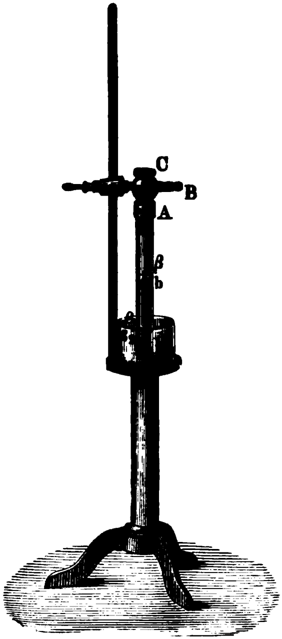

Fig. 87.

Two fine threads of black glass, β_1 and β_2, are fused around the lower part of the stem of the float. These two threads, together with the black glass button at the top, serve as marks.

If the tube containing the gas be pushed down so far into the mercury that a mark on the glass is tangent to the outer mercury surface, then the float which is inside the tube is no longer visible through the telescope.

If now the stopcock be opened and the gas allowed to escape through the opening in the platinum plate, the float rises, being carried up upon the surface of the mercury in the tube. If the level of the external mercury be observed through the telescope, the white glass tip of the float soon comes into the field, and informs the observer that the black button β will shortly appear. When this comes in sight the time is taken, the end of the timing being at that moment at which the mark β_2 comes into the field of the telescope; the near approach of β_2 is here shown by the appearance of β_1.

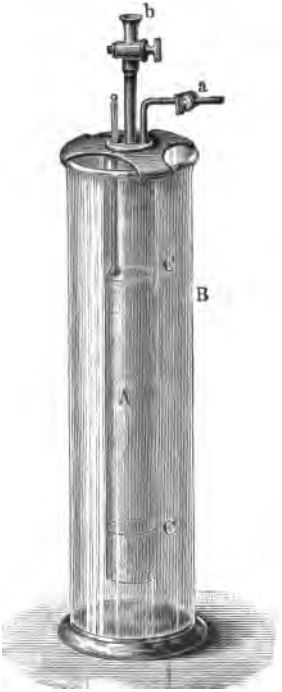

FIG. 88.

From these observations is obtained the rapidity of escape of a column of gas which, measured from β, has the length shown by the marks $\beta\beta_2$ on the float; moreover, the gases escape under the same differences of pressure in all of the experiments. The times taken by the different gases to escape through the fine opening in C give, when squared, the ratios of the specific gravities of the gases.

The gases must be dried, and the mercury must be pure and dry. An advantage of the Bunsen apparatus is that a determination can be made with a very small quantity of the gas.

N. H. Schilling has given the apparatus a very practical form for the examination of illuminating gas, where large amounts of the gas are usually available.

A (Fig. 88) is a glass tube of 40 mm. internal diameter and about 450 mm. long. The upper end is luted into a brass cover into which is inserted the tube *a* through which the gas is led in. In the middle of the plate is the escape tube *b*, and through another opening passes a thermometer. On the end of *b* is the perforated platinum plate. The inner cylinder has two marks, *CC*. The apparatus is filled with water.

To determine the specific gravity of an illuminating gas with this apparatus, the tube is first filled with air, and the time of escape of the air, under the prevailing temperature and pressure, is noted. The last trace of air is then removed by repeated drawing in and driving out the gas to be examined, and the time of escape of the illuminating gas is then observed. The squares of the values are directly proportional to the specific gravities of the gases. Since the specific gravity of air is usually taken as 1, the calculation is very simple.

A very convenient arrangement for the continuous and direct determination of the specific gravity is the gas-balance of Friedrich Lux.[1]

The instrument (Fig. 89) consists of a large bulb *A*, which is attached to one end of a lever, the other end gives directly on a scale the specific gravity of the gas. The lever is so made that the gas to be examined can be led through the tube *b* and through the hollow support into the bulb. The gas passes off through a second tube, which is also connected with the fulcrum of the lever. If a number of such balances are joined together, and if, between the balances, absorption apparatus for the various constituents is introduced, the composition of the gas can be read off directly from the positions of the different pointers. For use of this sort, Lux has devised a balance with two bulbs, by means of which the amount of one constituent in the gas can be directly read off.

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[1] To be obtained from Friedrich Lux, Ludwigshafen, Germany.

The results obtained by this instrument are of course influenced by the temperature and the variations of pressure, but nevertheless the apparatus is very well adapted for controlling the working of a gas plant.

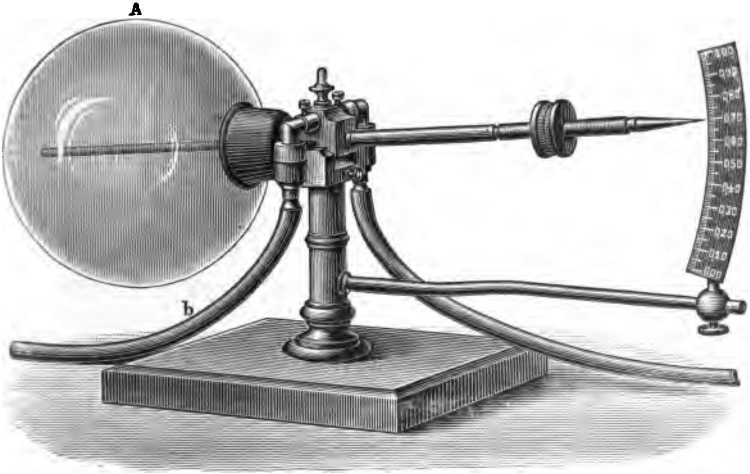

FIG. 89.

3. *The Determination of Tar, etc.*

For the determination of tar in unwashed gases, F. Tieftrunk uses the apparatus shown in Fig. 90. Winkler[1] describes this as follows:—

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II, p. 52.

"The glass cylinder *A* has a brass rim, and it can be tightly closed by means of a plate which is fastened with screws. To the tube *c* is attached a bell-shaped device *h*, which consists of perforated sheets of brass slipped over the tube. The distance between the rows of holes and also between the holes themselves is about 5 mm. The glass cylinder *A* is

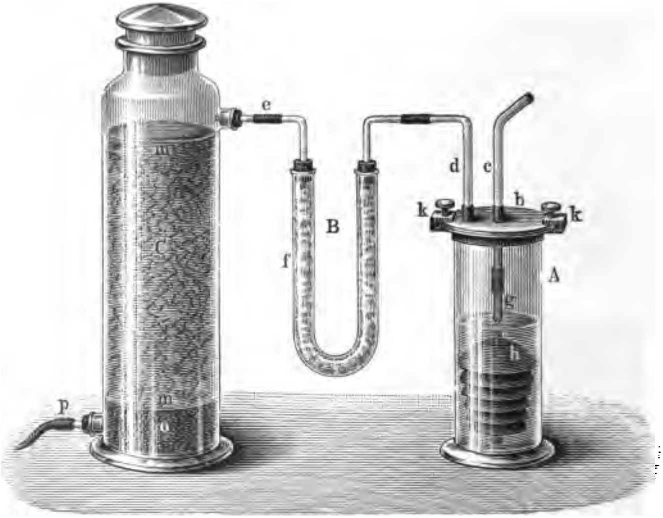

FIG. 90.

filled somewhat more than half full of alcohol of from 25 to 29 per cent by weight, the bell being entirely covered by the liquid. The alcohol takes up the tar which enters, but is said to hold back only traces of other constituents, such as benzene and naphthalene.

"The U-tube *B* is 12 mm. in diameter and 10 cm. long, and is filled with cotton. *C* is a glass-stoppered cylinder with two side openings. The lower part *o* of the cylinder is filled with cellulose; upon this lies a sheet of coarse filter paper, and above that is a layer of bog-iron ore, *mm*.

"The gas enters at *c* and passes out through *p* into an experimental gas-meter, and then into the aspirator. Before beginning the experiment, purified illuminating gas is allowed to pass through the washing apparatus for ten minutes to destroy the surface adhesion.

"The cotton in *B* should not be at all brown at the end of the experiment; if it is, it must be extracted with carbon disulphide.

"The solution thus obtained is placed in a weighed dish, and is allowed to evaporate. According to Tieftrunk's experience, one-third of the total oil passes off at the same time, and a correction is made for this after the residue has been weighed.

"When the experiment is ended, the apparatus is taken apart, the lid of the vessel *A* is raised, the tar adhering to the bell *h* is washed down with the aid of a wash-bottle filled with alcohol of 35° Tr., and the whole is allowed to stand for twelve hours. The solution is then filtered through a dried and weighed filter; the aspirator is used in this operation, but care is taken to turn it off when, toward the last, the liquid tar is brought upon the filter. After washing, the filter and its contents are placed in a desiccator, and after drying for twelve hours both are weighed. The weighing of the filter with and without the tar may conveniently be performed in a glass dish with steep sides. Some particles of tar remain clinging to the bell and the walls of the glass cylinder, in spite of the washing. As this cannot be avoided, the amount of tar adhering to the glass is determined by putting the apparatus — whose original weight must be known — together again, and drawing 100 liters of dry air through it. By this current of air, which lasts for about forty minutes, all water adhering to the walls is surely driven out, and the increase of weight of the apparatus gives the amount of the adhering tar. The weighings are made on a balance which, with a load of 1 kg., is sensitive to 0.01 g.

"Large volumes of gas are required in determining the tar by this method. Gases which contain much tar, and which are often still warm, are first passed through a long, weighed glass tube before they enter the absorption cylinder *A*. This tube slants toward *A* and is attached to *c*, and in it a sufficient cooling and condensation of the tar takes place. Most of the tar passes into *c* and collects at the bottom of *A*. 250 liters of gas are passed through the apparatus with a speed of from 30 to 40 liters an hour. If the gas to be examined has already passed through the condenser, or, in other words, if the gas sample is taken either before or after the scrubbers, 500 liters of the gas must be used, and it may be given a speed of from 50 to 60 liters per hour.

"Operating in this manner, Tieftrunk found in every 1000 cubic meters of gas —

Before the condensers . . .	150.0	to 200	kg. tar
" " scrubbers . . .	25.0	" 75	"
After the scrubbers	0.5	" 20	"

"These figures are only approximate. They vary greatly, and the cause of these variations lies in the character of the coal, the method of distillation, the form of the condensers, the action of the same, the form and action of the scrubbers, the size of the apparatus, .etc."

Bunsen[1] determines the gaseous hydrocarbons that are not properly gases, in purified illuminating gas, by slowly passing the gas, which is first carefully dried by calcium chloride, through a long glass tube bent slightly upward at its lower end, and then through a series of wash-bottles, the tube and wash-bottles being filled with absolute alcohol. The greater part of these liquid hydrocarbons which are present in the gas as vapours collect in the tube; only a very small amount is found in the alcohol of the last wash-bottle.

If the alcoholic contents of the washing apparatus be poured into a large excess of a concentrated solution of sodium chloride, the liquid hydrocarbons separate, without appreciable evolution of gas, as a milky cloud, which, upon standing, unites to a clear and colourless oily layer upon the surface of the salt solution. Three cubic meters of the Heidelberg illuminating gas, passed through 1 liter of alcohol, yielded a liquid which, after being freed from alcohol by washing with water and dried over calcium chloride, gave 36 g. of a clear liquid having the odour of pure benzene. This liquid began to boil between 80° and 90° C., and the boiling-point rose gradually to 140° C., only a very small residue boiling at a still higher temperature. By a number of fractional distillations the larger part of the total liquid was obtained as a product which boiled between 90° and

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[1] Bunsen, *Gasometrische Methoden*, 2d ed., p. 144.

100° C., and which upon being cooled to below 0° C. separated almost completely as pure benzene.

The hydrocarbons taken up by alcohol consisted chiefly of benzene. The hydrocarbons mixed with the benzene constituted so small a portion of the whole that their amounts could be wholly disregarded in the analysis as lying within the limits of experimental error.

In all of the illuminating gases, coming from the most varied sources, which Bunsen had opportunity to examine, not one contained less than from 4 to 12 times as much gas absorbable by sulphuric acid as there was benzene present. Hence that portion of illuminating gas which gives the lighting power consists chiefly of gaseous hydrocarbons.

The gases absorbable by sulphuric acid consist essentially of ethylene, propylene, and benzene vapours. All other hydrocarbons are here present in such small quantities that for analytical purposes they need not be considered.

If a more exhaustive analysis is to be made, we must examine, in addition to those hydrocarbons absorbable by alcohol, those products also which result from leading large amounts of the gas through sulphuric acid, the products formed by the action of chlorine and bromine, the constituents separable by ammonium cuprous chloride, and finally, if possible, the condensation products which separate out when the gas is compressed.

E. St. Claire-Deville[1] has made a large number of determinations of these hydrocarbon vapours by separating them through cooling to − 22° C. We have tested this method and also that proposed by Bunsen (p. 277), and have obtained the following results:[1] —

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[1] *Journal des usines à Gaz*, 1889, 18.

1427 liters of illuminating gas gave by Bunsen's method 15.4 ccm. of liquid hydrocarbons, from which, by fractional distillation and freezing, 3.5 ccm. of benzene was obtained.

1497 liters of illuminating gas gave by Deville's method 13 ccm. of liquid hydrocarbons, containing 5 ccm. benzene.

That the results by the two methods did not agree better is to be explained by the fact that it is almost impossible to keep the temperature constant at – 22° C. The experiments were made under the most favourable external conditions, *i.e.* during very cold days in winter, but in spite of the greatest care it was impossible to avoid considerable variations of temperature. More of the hydrocarbons were obtained by Bunsen's method than by that of Deville.

Further investigation showed that it is possible with 1 ccm. of alcohol to absorb and volumetrically determine the hydrocarbon vapour present in 100 ccm. of illuminating gas. In carrying out this determination, a sample of illuminating gas is measured over water which has been saturated with the gas. The burette is then connected with the mercury pipette of the form shown in Fig. 37, which contains above the mercury 1 ccm. of absolute alcohol. To avoid the absorption by the alcohol of gases other than these hydrocarbon vapours, it is well to first saturate the alcohol with the illuminating gas by drawing over about 100 ccm. of the gas into the pipette and then driving it out again. The saturation of the alcohol with the gas and the absorption of the hydrocarbon vapours by the alcohol are completely effected by simply passing the gas into the pipette and driving it out. The entrance of water into the pipette and the consequent dilution of the alcohol should be carefully avoided, because dilute alcohol does not completely absorb the vapours. The entrance of alcohol into the piece of rubber tubing attached to the capillary of the burette must also be avoided, for if alcohol should enter the burette, its tension would cause an appreciable error.

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[1] Hempel and Dennis, *Berichte der deutschen chemischen Gesellschaft*, **24**, 1162.

If a high degree of accuracy is desired, it is best to transfer the gas, after the absorption with alcohol and before measuring, into a second mercury pipette which contains 1 ccm. of water and to shake the gas for some minutes in this pipette. On transferring the gas again into the burette, the diminution in volume will accurately give the amount of hydrocarbon vapours present in the illuminating gas.

100 ccm. of Dresden illuminating gas when analysed with a burette filled with mercury and affording correction for temperature and pressure gave in two experiments —

0.74 per cent of hydrocarbon vapours
0.70 " " " "

To prepare a gas containing a known amount of hydrocarbon vapours, 90 ccm. of the above gas was shaken for a short time with benzene contained in a gas pipette. The volume was hereby increased to

93.1 ccm. After the absorption of the hydrocarbon vapours, the residue was 89.4 ccm.

In a second experiment, 90 ccm. of the gas shaken with benzene increased to 93.0 ccm. After the absorption the volume was 89.4 ccm.

These experiments show that with 1 ccm. of alcohol and 1 ccm. of water it is possible to quantitatively absorb the hydrocarbon vapours from a gas which contains about 3 per cent of these vapours.

The same gas as was used in the above experiments was analysed with the aid of a burette filled with water, but with the other details of the analysis exactly as above described, and the two results for the hydrocarbon vapours were 0.5 per cent and 0.63 per cent.

A sample of oil gas analysed in this manner gave 4.6 per cent of hydrocarbon vapours.

Since these vapours are quite soluble in potassium hydroxide, their determination must precede those of the other constituents of the gas. Otherwise the results for carbon dioxide will be too high, and those for the heavy hydrocarbons too low.

To determine the amount of benzene in a gas mixture, Harbeck and Lunge[1] led a large amount of the gas through an absorption apparatus which contained a mixture of concentrated nitric acid and sulphuric acid. Dinitrobenzene is formed, and, after dilution with water, it can be separated from the other substance by shaking with ether. It has been found that the substances formed by the action of ethylene and other gases and vapours upon the above-mentioned concentrated acids are easily soluble in water, and cannot be extracted with ether from an aqueous solution.

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[1] E. Harbeck and G. Lunge, *Zeitschrift für anorganische Chemie*, **16**, 41.

4. *The Volumetric Analysis*

For the volumetric analysis, a sufficient quantity of water must first be saturated with the illuminating gas, as directed on p. 53. The same must be done with the caustic potash pipette, unless a double pipette for solid and liquid reagents, which is filled with illuminating gas, is being used.

The hydrocarbon vapours are first absorbed with alcohol, then carbon dioxide with potassium hydroxide, then the heavy hydrocarbons with fuming sulphuric acid, then oxygen with phosphorus, and lastly carbon monoxide with the ammoniacal cuprous chloride solution. The residue, which consists of methane, hydrogen, and nitrogen, is measured, and is then led back into the cuprous chloride pipette, and a portion is taken for the explosion analysis.

With ordinary illuminating gas 12 ccm. of the residue suffice for the explosion.

These 12 ccm. are measured off in the gas burette, and enough air is drawn in to bring the mixture to about 100 ccm. In all these measurements the running down of the liquid must be most carefully waited for, because the amount of gas taken is so small that any errors that may be made are greatly multiplied.

The gas mixture is now burned in the explosion pipette. The gas is then transferred to the burette and the total contraction is measured. Then the carbon dioxide is absorbed with potassium hydroxide, and finally the oxygen in excess is absorbed with phosphorus. The last determination is made merely to be sure that a sufficient excess of oxygen was present in the combustion.

An analysis of illuminating gas is here given for the sake of illustration.

100 ccm. of illuminating gas measured off (see p. 37).

Shaken with alcohol and then with water, as described on p. 279; drawn back into the burette and measured at the end of three minutes (time allowed for the running down).

0.7 ccm. or per cent hydrocarbon vapours.

Passed into caustic potash pipette and drawn directly back into the burette; measured after three minutes. Measurement gave 4.1 ccm.; hence there was present 4.1 – 0.7 = 3.4 ccm. or per cent carbon dioxide.

Burette now connected by means of a dry piece of rubber tube and a dry capillary with the pipette containing fuming sulphuric acid. Gas driven over and drawn back at once into the burette. Gas now passed again into caustic potash pipette, and after being drawn back into the burette and allowed to stand three minutes, again measured. The measurement gave 8.4 ccm.; hence there were 8.4 – 4.1 = 4.3 ccm. or 4.3 per cent of heavy hydrocarbons present.

The gas now passed into phosphorus pipette and allowed to remain for three minutes; then drawn back into burette and measured at the end of three minutes. Reading gave 8.4 ccm.; hence no oxygen was present.

The gas was then passed into the pipette containing ammoniacal cuprous chloride which had been repeatedly used, and was shaken therein for two minutes. It was then drawn back into the burette and transferred at once to a second pipette containing ammoniacal cuprous chloride which had been used but little, and it was here shaken for three minutes. Drawn back into the burette and measured after three minutes; the reading was 18 ccm.; hence there was 18 ccm. $- 8.4 = 9.6$ ccm. or per cent carbon monoxide present.

The remaining 82 ccm. of gas was then passed back into the cuprous chloride pipette, and the pipette was closed with an ordinary pinchcock.

The water in the burette is poured out, the burette washed with hydrochloric acid and then with distilled water, and then filled with water which is saturated not with illuminating gas, but with air.

12 to 15 ccm. of the gas residue is now measured off into the burette. In this case 13.2 ccm. was taken.

So much air is then drawn in that the total volume of the gas residue taken and the air amounts to about 100 ccm. In this case it was 99.6 ccm.

This mixture is now brought into an explosion pipette filled with mercury, care being taken that the capillary remains full of water. The rubber connecting piece is closed by a strong pinchcock, and a piece of glass rod is slipped into the end of the rubber tube. The pipette is then vigorously shaken, the glass stopcock is closed, the pipette is connected with the poles of an induction coil, and by lowering the dip battery the mixture is exploded. The glass stopcock is at once opened and the remaining gas is transferred without delay to the burette, and, after three minutes, measured. The result here was 78 ccm.

The total contraction was therefore $99.6 - 78 = 21.6$ ccm.

The gas remaining from the combustion is now passed into the caustic potash pipette, drawn directly back into the burette, and, after three minutes, measured. The reading was 73.2 ccm. Hence by the combustion $78 - 73.2 = 4.8$ ccm. of carbon dioxide was formed.

Although this gave all the data necessary for the calculation of the analysis, the remaining gas was nevertheless passed into the phosphorus pipette in order to be sure that an excess of oxygen was present in the combustion, or, in other words, that the gas was completely burned. The measurement gave 70.2 ccm.

Hence there was $73.2 - 70.2 = 3$ ccm. of oxygen in excess.

In the combustion of the marsh-gas its own volume of carbon dioxide is formed, so that in the 13.2 ccm. of the gas residue taken for the explosion there were 4.8 ccm. of marsh-gas.

The marsh-gas in the total gas residue of 82 ccm. is found by the proportion —

$$13.2 : 82 = 4.8 : x,$$
$$x = 29.8 \text{ per cent marsh-gas.}$$

Since marsh-gas in burning unites with twice its volume of oxygen, the contraction which has resulted from the combustion of the hydrogen is found by subtracting twice the volume of the carbon dioxide found from the total contraction. $21.6 - (2 \times 4.8) = 12$ ccm. contraction due to the burning of hydrogen.

One volume of hydrogen unites, in burning, with one-half its volume of oxygen; hence the volume of the hydrogen is found by multiplying 12 by $\frac{2}{3}$. Thus the 13.2 ccm. of the gas residue taken for the explosion contained 8 ccm. of hydrogen. The total amount of hydrogen is given by the proportion —

$$13.2 : 82 = 8 : x,$$
$$x = 49.6 \text{ per cent hydrogen.}$$

The nitrogen is found by subtracting the sum of all the other constituents from 100. This gives 2.6 per cent.

Hence the illuminating gas contained —

0.7	per cent	hydrocarbon vapours
3.4	"	carbon dioxide
4.3	"	heavy hydrocarbons
0.0	"	oxygen
9.6	"	carbon monoxide
29.8	"	methane
49.6	"	hydrogen
2.6	"	nitrogen.
100.0		

In this analysis the following apparatus was used: —

One gas burette (Fig. 27, p. 35).

A mercury pipette (Fig. 37, p. 67).

One gas pipette for fuming sulphuric acid (Fig. 82, p. 229).

Two double absorption pipettes for cuprous chloride (Fig. 33, p. 51).

A gas pipette for phosphorus (Fig. 32, p. 49).

An explosion pipette (Fig. 63, p. 130).

A small induction coil (Fig. 69, p. 137).

A dip battery (Fig. 68, p. 135).

A number of capillary connecting tubes.

A three-minute sand glass.

In place of the absorption pipette there may be used either a Winkler-Dennis combustion pipette (Fig. 70, p. 138) or a Drehschmidt platinum capillary (Fig. 71, p. 140).

With careful work, the determinations of the hydrocarbon vapours, carbon dioxide, heavy hydrocarbons, oxygen, and carbon monoxide are exact to about 0.2 per cent, but the experimental errors in the analysis of the marsh-gas, hydrogen, and nitrogen may rise to 1 per cent. The reason for this lies in the fact that only small quantities of gas can be taken for the explosion, and that all results are then calculated for a gas volume about six times as large. In the above example the proportion was 13.2 : 82.

It would be unadvisable, and would also lead to no greater accuracy, to explode very large volumes, because the error caused by the unequal heating of the gas mixture increases as the quantity of gas increases.

Direct comparison of two analyses, one of which was made entirely over mercury, while the other was carried out in a burette filled with water and an explosion pipette filled with mercury in the manner just described, showed that the determination of carbon dioxide by the latter method was quite exact.

As it was suspected that the residue of marsh-gas, hydrogen, and nitrogen might contain, in addition to these gases, higher members of the marsh-gas series, experiments were made to answer the question.

Mercury was employed as confining liquid and the greatest care was used. The result showed that when the hydrogen had first been absorbed by palladium, the carbon dioxide formed in the explosion corresponded exactly to the oxygen used and the contraction observed. We may hence conclude that in ordinary illuminating gas there is no appreciable amount of ethane present with the methane.

The determination of hydrogen may be made more exactly by absorption with palladium (see p. 181). Yet many experiments have shown that the accuracy attained by making use of the fractional combustion of hydrogen is not greater than in the above procedure.

The following analysis is given to illustrate the calculation of the analysis when the hydrogen is fractionally burned.

The direct absorption gave —

0.6	per cent	hydrocarbon vapours
3.4	"	carbon dioxide
4.4	"	heavy hydrocarbons
0.3	"	oxygen
10.1	"	carbon monoxide.

The residue of hydrogen, methane, and nitrogen amounted to 81.2 ccm. This was transferred to a pipette and 40.5 ccm. were measured off in a burette for the fractional combustion of the hydrogen. To this was added air — in this case 58.7 ccm. — and the mixture was passed into a pipette filled with water. Then more air was measured off in the burette and transferred to the pipette, so that the total amount of air added would without doubt be sufficient for the combustion of the hydrogen. In this second measurement 16.1 ccm. of air were taken, so that the total amount of gas taken for the fractional combustion was —

$$40.5 + 58.7 + 16.1 = 115.3 \text{ ccm.}$$

The gases were vigorously shaken in the pipette to thoroughly mix them, and were then fractionally burned by leading them over 0.5 g. of palladium.

The volume after the combustion was 81 ccm.; hence the contraction was —

$$115.3 - 81 = 34.3 \text{ ccm.},$$

corresponding to 22.9 ccm. of hydrogen, the total amount of hydrogen being found by the proportion —

$$40.5 : 81.2 = 22.9 : x,$$
$$x = 45.9 \text{ per cent hydrogen.}$$

To determine the methane, 19.9 ccm. of the residue of hydrogen, methane, and nitrogen were taken and, together with 110 ccm. of air, were transferred to the explosion pipette. The gases were well mixed, and were then exploded, freed from carbon dioxide in the potassium hydroxide pipette, and measured. There remained 90.5 ccm. The contraction was —

$$110 + 19.9 - 90.5 = 39.4 \text{ ccm.}$$

From the determination of the hydrogen by the fractional combustion we know that in 19.9 ccm. of the residue, by hydrogen would cause a contraction of 16.9 ccm. ($40.5 : 19.9 = 34.3 : x$, $x = 16.9$); hence the contraction due to the methane is equal to 39.4 − 16.9 = 22.5 ccm., and the volume of the methane itself is 7.5 ccm.

The per cent of methane is —

$$19.9 : 81.2 = 7.5 : x,$$
$$x = 30.6 \text{ per cent marsh-gas.}$$

The nitrogen determined by difference as before is 4.7 per cent, so that the composition of the gas was as follows: —

0.6	per cent	hydrocarbon vapours
3.4	"	carbon dioxide
4.4	"	heavy hydrocarbons
0.3	"	oxygen
10.1	"	carbon monoxide
45.9	"	hydrogen
30.6	"	marsh-gas
4.7	"	nitrogen.

EXAMPLE TO ILLUSTATE THE METHOD OF PROCEDURE AND THE CALCULATION IN THE ANALYSIS OF GENERATOR GAS

In addition to the apparatus used for the analysis of illuminating gas, a hydrogen pipette (p. 131) is here necessary, provided a Winkler-Dennis combustion pipette or a Drehschmidt platinum capillary is not used.

The manipulation differs merely as concerns the combustion of the unabsorbable residue.

A generator gas made from brown coal in a shaft generator gave —

3.4	per cent	carbon dioxide
0.8	"	heavy hydrocarbons
0.3	"	oxygen
25.4	"	carbon monoxide.

The residue of marsh-gas, hydrogen, and nitrogen amounted to 70.1 ccm. The gas mixed with air would not explode, hence hydrogen was added.

The mixture that was exploded consisted of —

15.3	ccm.	of the gas residue
84.0	"	air
10.5	"	hydrogen.

After the explosion the volume was —

89.2 ccm.,

and the contraction was —

$$(15.3 + 84 + 10.5) - 89.2 = 20.6 \text{ ccm.}$$

The 10.5 ccm. of hydrogen added, used up in its combustion 5.25 ccm. of oxygen, so that 15.75 ccm. must be subtracted from the total contraction to ascertain the contraction resulting from the hydrogen and marsh-gas in the generator gas.

This gives 4.85 ccm. contraction.

The absorption of the carbon dioxide formed in the combustion gave 1.3 ccm.

Since this volume is equal to that of the methane, the following proportion gives the per cent of the latter: —

$$15.3 : 70.1 = 1.3 : x,$$
$$x = 5.3 \text{ per cent marsh-gas.}$$

The marsh-gas unites with twice its volume of oxygen, so that the contraction resulting from the combustion of the hydrogen is found by subtracting twice the volume of the carbon dioxide formed from the total contraction —

$$4.85 - (2 \times 1.3) = 2.25 \text{ ccm.}$$

Hence the 15.3 ccm. of the gas residue taken for the explosion contained —

$$2.25 \times \tfrac{2}{3} = 1.5 \text{ ccm. hydrogen.}$$

and the total amount of hydrogen is —

$$15.3 : 70.1 = 1.5 : x,$$
$$x = 6.8 \text{ ccm. or per cent hydrogen.}$$

The nitrogen, by difference, was 57.4 per cent. Hence the generator gas contained —

3.4	per cent	carbon dioxide
0.8	"	heavy hydrocarbons
0.3	"	oxygen
25.4	"	carbon monoxide
5.9	"	marsh-gas
6.8	"	hydrogen
57.4	"	nitrogen.

Berthelot's method for the analysis of illuminating gas, in which the heavy hydrocarbons are separated from benzene by bromine, and the benzene then absorbed by fuming nitric acid, has been found by F. P. Treadwell and H. N. Stokes[1] to be impracticable. On the one hand, bromine absorbs some benzene in addition to the ethylene, and, on the other hand, fuming nitric acid oxidises carbon monoxide.

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[1] *Berichte der deutschen chemischen Gesellschaft*, **21**, 3131.

They found it possible to completely oxidise carbon monoxide by shaking the gas for a long time with fuming nitric acid.

At the present time there exists no simple method for the separation of the heavy hydrocarbons.

The accuracy of the combustion analysis for the determination of hydrogen and methane may be greatly increased by the use of the method of Dennis and Hopkins.[1] This procedure permits of the use of large volumes of gas, and effects the combustion by means of pure oxygen, thus avoiding to a great degree the possibility of the formation of oxides of nitrogen. The combustion pipette employed is that described on p. 138, Fig. 70. A measured quantity of the gas to be burned is introduced into this pipette, and there is measured off in the gas burette a quantity of oxygen more than sufficient to completely burn the gas. The burette is then connected with the pipette by the usual bent capillary tube (see Fig. 91), and the level-bulb of the pipette and the level-tube of the burette are placed at such heights that the gases in both pipette and burette are approximately under atmospheric pressure. A screw pinchcock *k* which has previously been placed upon the rubber tube joining the burette with its level-tube is now tightly screwed down so as to prevent, for the present, any movement of the mercury in the burette. The level-tube is now placed at such a height that when the screw pinchcock *k* is opened the mercury will rise to the top of the burette but will not pass over into the pipette. The pinchcocks *o*, *o* on the connections between the burette and pipette are now opened, and the electric current, which should be just strong enough to maintain the spiral at a red heat, is turned on. Any electrical apparatus furnishing a current of sufficient strength to heat

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[1] *J. Am. Chem. Soc.*, **21**, 398; *Zeitschr. f. Anorgan. Chemie*, **19**, 179.

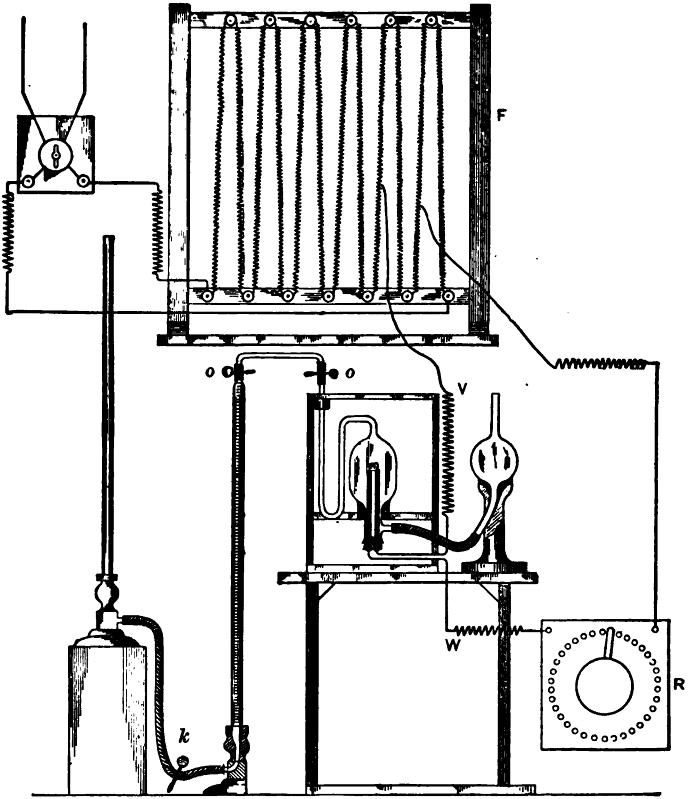

Fig. 91.

the platinum spiral to redness may, of course, be employed. If the current from a dynamo or storage battery is at the operator's disposal, the arrangement shown in Fig. 91 can be recommended as being both simple and convenient. The current is passed through the resistance frame *F*. (A small frame carrying German silver wire about 1.5 mm. in diameter may be used.) The terminals on the combustion pipette are connected with the frame by means of the flexible wires *V* and *W*, the ends of these wires being simply hooked into the coiled wire of the frame. The current passing through the platinum spiral can then be varied at will by simply hooking the end of *W* into the resistance coil at a greater or less distance from *V*. Instead of connecting *V* and *W* directly with the resistance frame in the manner described, it will be found convenient to introduce into the circuit the rheostat *R*. This will enable the operator to control easily and instantly the current flowing through the platinum spiral.

When the spiral has been brought to the proper temperature the screw pinchcock *k* is carefully opened and a slow and steady current of oxygen is passed over into the pipette. From 10 to 20 ccm. of oxygen per minute may be introduced, but the amount is, of course, somewhat dependent upon the length and temperature of the spiral. The combustion takes place quietly without the appearance of a flame, and if the operation is properly conducted there is no possibility of an explosion, since the combustible gas and the oxygen are in separate vessels and are made to combine as fast as they mix.

Nevertheless, a screen of heavy glass is always placed between the pipette and the operator to insure protection for the face in case of possible accident. This precaution should be invariably taken in all combustion or explosion analyses of gas mixtures. After the oxygen has been passed into the pipette, the spiral is kept at a red heat for about one minute to insure complete combustion of the gas. When, however, hydrogen alone is being burned, the combustion is complete almost as soon as sufficient oxygen has been introduced. When the combustion is finished, the residual gas is passed back into the burette and measured.

The volume of gas which may be taken for the combustion is limited only by the capacity of the measuring burette, but for convenience in handling neither the combustible gas, the oxygen required, nor the residue after combustion is allowed to exceed 100 ccm. The volume of gas in the pipette at any time during the combustion should be sufficient to prevent the mercury from rising and covering the spiral, or short-circuiting the current. This would take place if pure hydrogen were burned by adding pure oxygen, but the difficulty in this case is avoided by introducing into the 100 ccm. of hydrogen about 95 ccm. of a mixture of equal parts of oxygen and air.

The results obtained in the determination of hydrogen by this method have already been given on p. 177.

Experiments have also been made upon the simultaneous combustion and determination of hydrogen and methane in illuminating gas.

Illuminating gas was passed into fuming sulphuric acid to remove hydrocarbon vapors and heavy hydrocarbons, then shaken with alkaline pyrogallol to remove oxygen, carbon dioxide, and the fumes of the sulphuric acid, and finally shaken, first with old and then with fresh cuprous chloride, to remove carbon monoxide. Measured portions of the residue which now contained hydrogen, methane, and nitrogen were then introduced into the combustion pipette and burned with oxygen in the manner described above. It is also possible to determine the three gases — carbon monoxide, hydrogen, and methane — by one combustion.

	I	II	III	IV	V
	ccm.	ccm.	ccm.	ccm.	ccm.
Gas residue taken	61.4	64.50	67.00	64.0	65.7
Oxygen taken	98.5	96.55	98.55	97.6	100.0
Total	159.9	161.05	165.55	161.6	165.7
Residue after combustion	58.8	54.95	55.30	56.3	57.6
Contraction	101.1	106.10	110.25	105.3	108.1
Residue after absorbing CO_2 in KOH pipette	34.3	29.15	28.60	30.7	31.4
Carbon dioxide found	24.5	25.80	26.70	25.6	26.2
	Per cent	Per cent	Per cent	Per cent	Per cent
Hydrogen	56.4	56.30	56.60	56.4	56.5
Methane	39.9	40.00	39.90	40.0	39.9
Nitrogen (diff.)	3.7	3.70	3.50	3.6	3.6

A mixture of these gases together with nitrogen was obtained by extracting from illuminating gas by means of the usual absorbents only the hydrocarbon vapours, heavy hydrocarbons, oxygen, and carbon dioxide. A measured volume of the residue was transferred to the combustion pipette and burned with oxygen. The residual gas was then passed back into the burette, measured to ascertain the contraction, and then passed into the caustic potash pipette to absorb the carbon dioxide, and again drawn back and measured. In the meantime a known volume of hydrogen had been brought into the combustion pipette. This was then connected with the burette which now contained nitrogen and the unconsumed oxygen, the current was turned on, and the oxygen was passed over into the hydrogen. From the resulting contraction the excess of oxygen was ascertained, and the difference between this and the oxygen first taken gives the amount of oxygen consumed in the combustion of the carbon monoxide, hydrogen, and methane.

Having thus ascertained the contraction resulting from the combustion, the volume of carbon dioxide formed, and the amount of oxygen consumed, we have all the data necessary for the calculation of the amounts of carbon monoxide, hydrogen, methane, and nitrogen existing in the original mixture. The reactions which take place in the combustion and the volume changes due to these reactions are the following:[1] —

$$\underset{\text{2 vols.}}{2\,CO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2\,CO_2}.$$

Contraction in burning 2 vols. CO = 1 vol.

Hence contraction for 1 vol. CO = $\frac{1}{2}$ vol.

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[1] Cf. Vignon, *Bull. Soc. Chim.*, 1897, 832.

$$\underset{\text{2 vols.}}{2\,H_2} + \underset{\text{1 vol.}}{O_2} = \underset{\text{liquid.}}{2\,H_2O}.$$

Contraction in burning 2 vols. H = 3 vols.
Hence contraction for 1 vol. H = 1.5 vols.

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2\,O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{liquid.}}{2\,H_2O}.$$

Contraction in burning 1 vol. CH_4 = 2 vols.

From the above equations we have —

Contraction = $\frac{1}{2}$ CO + $\frac{3}{2}$ H + 2 CH_4.

Carbon dioxide formed = CO + CH_4.

Oxygen consumed = $\frac{1}{2}$ CO + $\frac{1}{2}$ H + 2 CH_4.

From these last three equations a variety of formulas for the calculation of the various components of the original mixture may be derived. Noyes and Shepard give —

(1) H = Contraction minus oxygen consumed.
(2) CO = $\frac{2}{3}$(2 CO_2 + $\frac{1}{2}$ H minus oxygen consumed).
(3) $CH_4 = CO_2 - CO$.
(4) N = Original volume − (H + CO + CH_4).

Instead of (2) and (3) we may also use —

$$CO = CO_2 - CH_4.$$

$$CH_4 = \frac{2\ \text{Contraction} - CO_2 - 3\,H}{3}.$$

If no nitrogen is present in the original mixture the following equations of Vignon may be employed, *V* representing the volume of the gas mixture taken for the combustion.

$$H = V - CO_2.$$
$$CO = \tfrac{1}{3}\,CO_2 + V - \tfrac{2}{3}\text{ contraction.}$$
$$CH_4 = \tfrac{2}{3}\,CO_2 + \tfrac{2}{3}\text{ contraction} - V.$$

	I	II	III	IV
	ccm.	ccm.	ccm.	ccm.
Volume of gas residue taken	**83.45**	**85.05**	**83.05**	**86.95**
Oxygen added	97.65	96.25	97.90	99.95
Total	181.10	181.30	180.95	186.90
Volume after combustion	49.30	46.95	49.75	49.50
Contraction resulting from combustion	**131.80**	**134.35**	**131.20**	**137.40**
Volume after absorption of carbon dioxide	13.05	10.15	13.75	12.00
Volume of carbon dioxide formed in the combustion	**36.25**	**36.80**	**36.00**	**37.50**
Hydrogen taken for determination of excess of oxygen	50.65	40.80	41.35	40.90
The preceding + volume remaining after absorption CO_2	63.70	50.95	55.10	52.90
Volume after combustion	32.15	28.30	21.20	24.75
Contraction resulting from this combustion	31.55	22.65	33.90	28.15
Oxygen in excess ($\tfrac{1}{3}$ preceding contraction)	10.52	7.55	11.30	9.38
Oxygen consumed in combustion of CO, H, and CH_4	**87.13**	**88.70**	**86.60**	**90.57**

From the above experimental results the calculated percentages of the various gases are as follows : —

	I	II	III	IV
	Per cent	Per cent	Per cent	Per cent
Carbon monoxide .	6.2	6.1	6.2	6.0
Hydrogen	53.5	53.7	53.7	53.9
Methane	37.3	37.2	37.2	37.1
Nitrogen (difference)	3.0	3.0	2.9	3.0

The determination of oxygen in the method just described takes fully as much time as the direct absorption of carbon monoxide, and it is therefore usually advisable to first separate and determine the latter gas by means of cuprous chloride.

In carrying on the various combustions by which the above results were obtained, it was observed that a much stronger current is required to maintain the spiral at a red heat in an atmosphere of gases of low molecular weight than is needed with heavier gases, this being probably due to the different thermal capacities of the various gases, and to the varying velocities of the different gas molecules. This phenomenon is especially marked in the combustion of hydrogen, for with this gas it is necessary to markedly decrease the strength of the current as the combustion proceeds, since otherwise a current which will heat the spiral only to redness in the atmosphere of hydrogen at the beginning, is liable to melt the platinum wire in the mixture of nitrogen and oxygen which remains after the combustion is completed.

An interesting reaction which was observed during the progress of the work is that a mixture of methane and water vapour, when heated by the spiral, reacts as follows:—

$$CH_4 + H_2O = CO + 3\,H_2.$$[1]

According to this equation 1 volume of methane should yield 4 volumes of the mixture of carbon monoxide and hydrogen. On actual experiment it was found that 24.1 ccm. of impure methane expanded to 74.5 ccm., from which cuprous chloride absorbed 16.5 ccm. This 16.5 ccm. of carbon monoxide shows that an equal volume of methane was present in the original gas, and, according to the above equation, the 16.5 ccm. of methane, on being heated in the presence of the water vapour, should show an increase in volume of 49.5 ccm. The expansion observed was 50.4 ccm., a result which is sufficiently close to sustain the above reaction. That the observed expansion does not agree more nearly with the calculated increase in volume is doubtless due to the fact that at high temperatures carbon monoxide reacts with water vapour, forming carbon dioxide and hydrogen.[2] That this actually does take place was ascertained by introducing into the combustion pipette 79.75 ccm. of pure, moist carbon monoxide, and heating the spiral for five minutes. The volume was thereby increased to 82.75 ccm. from which 3.05 ccm. of carbon dioxide were absorbed by potassium hydroxide.

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[1] Several years ago Coquillion observed that the same reaction takes place in the presence of a red-hot palladium spiral. — *Compt. rend.*, **86**, 1198.

[2] Cf. Dixon, *J. Chem. Soc.*, **49**, 99, 100.

5. *The Determination of Sulphur*

The sulphur in illuminating gas is present either as hydrogen sulphide, or as carbon disulphide, or as some other combination with carbon and hydrogen.

Purified illuminating gas should be free from hydrogen sulphide. The hydrogen sulphide is determined by leading the gas through a suitable absorption apparatus containing a solution of lead nitrate. The resulting lead sulphide is filtered off, oxidised in a porcelain crucible with nitric acid, treated with a drop of sulphuric acid, evaporated to dryness, ignited, and weighed.

Bunte[1] determines the hydrogen sulphide in unpurified gas by measuring off 100 ccm. of the gas in one of the gas burettes devised by him, and then allowing a solution of iodine to enter until it is no longer decolourised —

$$H_2S + I_2 = S + 2\,HI.$$

The iodine solution is prepared by dissolving 1.134 g. of pure iodine in 1 liter of water. 1 ccm. of this solution corresponds to 0.1 ccm. of hydrogen sulphide at 0° and 760 mm. pressure. The sharpness of the reaction can be increased by adding starch-paste, the iodine being then added until the characteristic blue colour of the iodide of starch is seen.

Hydrogen sulphide can be separated from carbon dioxide by means of manganese dioxide, this substance holding back the hydrogen sulphide.

Carbon disulphide can be separated either as potassium xanthogenate, or as the tri-ethyl phosphorus compound.

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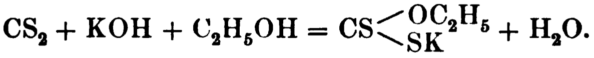
[1] Bunte, *Journal für Gasbeleuchtung*, 1888, **31**, 898.

A. Vogel has found[1] that the smallest amounts of carbon disulphide, when brought into a solution of potassium hydroxide in alcohol, form potassium xanthogenate —



$$CS_2 + KOH + C_2H_5OH = CS\begin{matrix}\diagup OC_2H_5\\ \diagdown SK\end{matrix} + H_2O.$$

To determine carbon disulphide, the gas is led through an alcoholic solution of potassium hydroxide, the alcohol is evaporated, acetic acid is added to slight acid reaction, and a dilute solution of cupric acetate is added. If carbon disulphide was present, a yellow precipitate results.

A. W. Hofmann has given[2] an exceptionally sharp reaction for carbon disulphide. If a gas containing traces of carbon disulphide be led through a suitable absorption apparatus containing a solution of tri-ethyl-phosphine in ether, the liquid turns red, and after the evaporation of the ether beautiful ruby-red crystals remain —

$$P(C_2H_5)_3 + CS_2 = P(C_2H_5)_3CS_2.$$

Since, however, a not inconsiderable portion of the sulphur in illuminating gas is present neither as hydrogen sulphide nor as carbon disulphide, a determination of the total sulphur of the gas is usually made.

After many experiments, the author is of the opinion that of the numerous methods which have been proposed for the determination of the total sulphur in illuminating gas, the following is the best. This is essentially the method of Drehschmidt, except that in the place of a Bunsen burner which burns in a cylindrical mantle of glass there is used a small flame burning in the interior of a large glass flask. This arrangement is preferable to that of Drehschmidt because the latter in the hands of students is frequently broken.

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[1] A. Vogel, *Annalen der Chemie und Pharm.*, 1853, 369.

[2] A. W. Hofmann, *Ibid.*, **115**, 293.

The illuminating gas under examination is measured in an experimental gas-meter and then passes through a short piece of rubber tubing *b* and the glass tubing *c* into the flask *A*, Fig. 92. *b* is provided with a screw pinchcock. The tube *c* is of hard glass, is about 5 mm. in diameter, is bent somewhat downward after it enters the flask and is drawn out at the end to a small opening. The neck of the receiving flask *A* is drawn down in the flame of the blast lamp to a small tube which is connected at *d* by means of a piece of rubber tubing with the absorption apparatus *DD*. The three-way glass tube *e* is inserted in the tubulus of the flask and is held in position in the neck by a piece of rubber tubing or a rubber stopper with a large opening. The side arm of the three-way piece *e* is joined by the rubber tube *f* to the cylinder *B*. This cylinder is filled with pieces of pumice-stone upon which there is allowed to drop a solution of potassium hydroxide from a separatory funnel. The air drawn into the apparatus must pass through this tower and is there freed from any hydrogen sulphide which may be present in the air of the laboratory. *g* is connected with an ordinary water suction pump.

In each absorption bottle *DD* is placed 20 ccm. of a 5 per cent solution of potassium carbonate. To the contents of the first two bottles there is added a few drops of bromine to oxidise the sulphur dioxide to sulphuric acid.

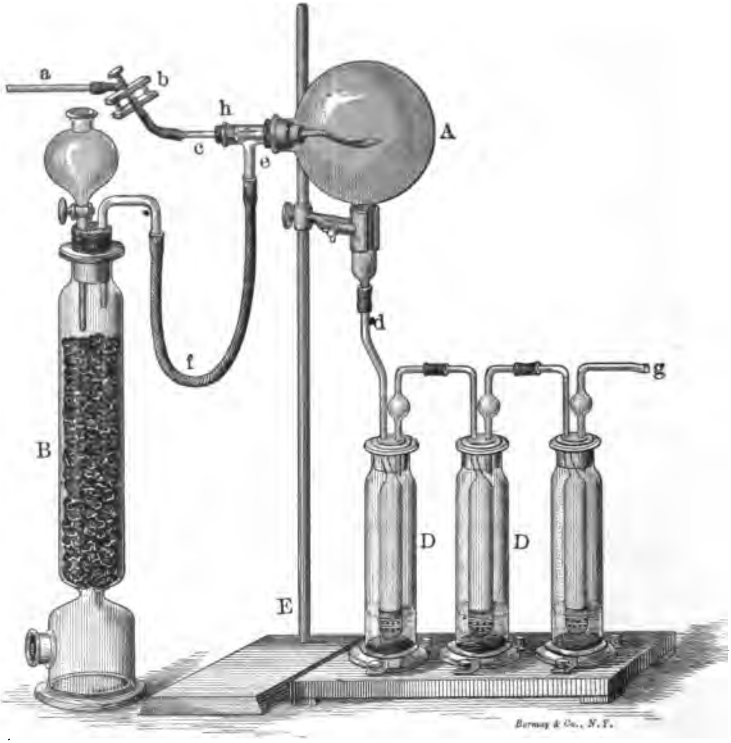

FIG. 92.

The illuminating gas should be allowed to pass through the gas-meter for some time previous to the beginning of the determination, to make sure that the meter is completely filled with the gas under examination.

When the apparatus has thus been prepared for the determination, the water suction pump is started, and a rapid current is drawn through the purifying cylinder *B*, the flask *A*, and the bottles *DD*. The tube *c* is withdrawn from the flask, and the gas is ignited at its outlet. The screw pinchcock *b* is closed until the flame is about 1 cm. long, and *c* is then introduced into *A* and the cork *h* is firmly inserted into position. *c* should be moved in or out through *h* until the flame burns in the middle of the flask. It should lie slightly below the lower side of the tubulus of the flask. In this position the flame will burn quietly for hours, but if it is above the tubulus it will go out, because in the upper part of the flask the products of combustion are not removed with sufficient rapidity by the entering current of air. By means of the screw pinchcock *b* it is easy to so regulate the flame as to cause it to burn with sharply defined edges, thus insuring complete combustion of the illuminating gas.

When about 50 liters of the gas have been burned the process is stopped, the flask *A* is rinsed out into a beaker, and the contents of the bottles *DD* are also transferred to a beaker. The liquid is acidified with hydrochloric acid, is then boiled to expel the bromine, and the hot solution is precipitated with barium chloride. The barium sulphate is separated and weighed in the usual manner, and the sulphur found is calculated for 100 ccm. of gas at 10° C. and 760 mm. pressure. If 50 liters have been used for the determination, and if *t* denotes the temperature of the gas, f the tension of aqueous vapour at this temperature, B the barometric pressure, and p the weight of the barium sulphate, then the amount of sulphur S in 100 cubic meters of the gas is —

$$S = 2000.\,p.\,0.13748 \times \frac{750.8}{283} \times \frac{273+t}{B-f}$$
$$= p\ 729.47 \times \frac{273+t}{B-f}.$$

Bromine frequently contains sulphuric acid as an impurity, and it is therefore necessary to make a second solution exactly similar to that which has been placed in the bottles *DD*, and to determine the sulphuric acid which this solution contains, subtracting then the amount thus found from that resulting in the regular analysis.

6. *The Determination of Ammonia*

Tieftrunk determines ammonia[1] by drawing the gas through a suitable absorption apparatus containing normal acid, and measuring the volume of gas with a meter.

If unwashed gas is being examined there is introduced between the meter and the absorption apparatus a tube filled with cotton, and a wash-bottle containing a solution of sugar of lead neutralised with acetic acid. These serve to hold back the hydrogen sulphide and the tar.

By titrating back the normal acid the amount of ammonia is found.

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II, p. 287.

If the gas contains very much tar, the normal acid must be filtered before the titration. In this case a measured portion of the solution is taken for the titration, and the total ammonia is calculated therefrom.

7. *The Determination of Carbon Dioxide*

The carbon dioxide can be determined with great exactness with the apparatus devised by Rüdorff.[1] This consists of a three-necked bottle *A* (Fig. 93): in one neck the manometer *B*, filled with a solution of indigo, is inserted; in the second neck the glass stopcock pipette *C*, graduated in tenths; and in the third neck either a single glass stopcock or a double-bore stopper carrying two tubes, one of which reaches to the bottom of the bottle, while the other ends just below the stopper.

The exact contents of the bottle must be known. In making the determination, illuminating gas is led into the bottle until all of the air is driven out, the lighter gas being introduced at the top of the bottle and the heavier air passing out below. The stopcocks are now closed, and the manometer is brought to zero by carefully allowing some of the gas which is in the bottle, and which is under pressure, to escape. If now a solution of potassium hydroxide be allowed to drop from the pipette into the bottle, the carbon dioxide will be absorbed. The volume of the carbon dioxide present can be read off directly from the pipette, if, after the absorption, the manometer is again brought to zero by admitting more caustic potash.

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[1] *Pogg. Annal.*, **125**, 75; also *Zeitschrift für analyt. Chemie*, **4**, 231.

In this determination the gas must of course be free from hydrogen sulphide. If this is not the case, the gas is passed through manganese dioxide before entering the apparatus. To avoid changes of tem-

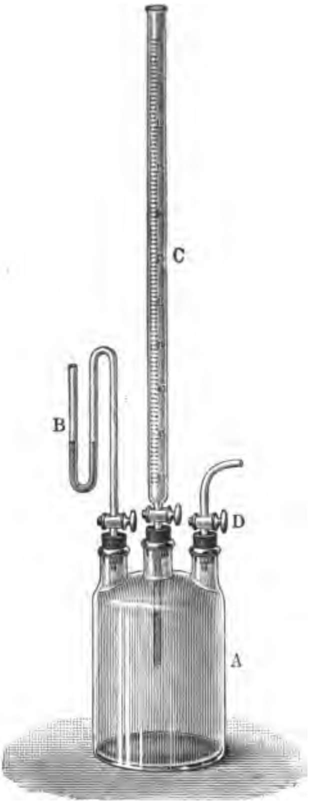

Fig. 93.

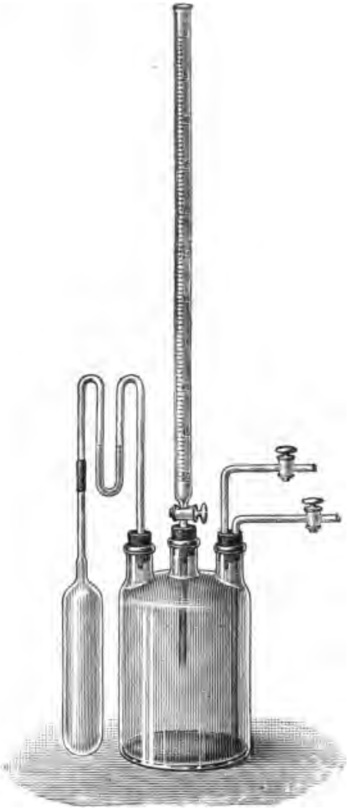

Fig. 94.

perature it is advisable to place the apparatus in a vessel of water during the experiment.

It is self-evident that the apparatus in this form is influenced by changes of temperature and pressure of the atmosphere. It can be made independent of these by attaching a Pettersson compensating tube to the manometer, as in Fig. 94.

CHAPTER III

ACETYLENE GAS

THE growing use of acetylene gas as an illuminant, the ease with which it can be prepared from calcium carbide, and the danger which may result from the use of impure gas, or badly constructed apparatus, or improper handling, all combine to make the correct analysis of this gas or of mixtures containing it a matter of considerable importance.

It should be borne in mind that trustworthy results cannot be obtained by taking a small piece of calcium carbide from the lot which is to be used for the preparation of acetylene, bringing this sample into a small, experimental apparatus, setting free the acetylene, and analysing the gas. Commercial calcium carbide is so far from being uniform in composition that it is absolutely essential to prepare an average sample from a large amount of the substance; but the calcium carbide itself is very hard and it cannot be pulverised without appreciable loss, owing to the ease with which it decomposes. It is therefore best to analyse the gas which has been set free from a considerable portion of the carbide.

Commercial calcium carbide is frequently contaminated with free calcium, calcium phosphide, aluminium carbide, and aluminium sulphide. Hence in the analysis of acetylene the following gases have to be considered: —

1. Acetylene.
2. Oxygen.
3. Nitrogen.
4. Hydrogen.
5. Methane.
6. Phosphine.
7. Hydrogen sulphide.
8. Silicon hydride.

In carrying out an analysis the acetylene is first absorbed by fuming sulphuric acid in the pipette shown in Fig. 82. It is here necessary to pass the gas repeatedly into the pipette until no diminution in volume is noticed upon measuring the residual gas in the burette. Before making the final measurement, the gas must, of course, be passed over into the caustic potash pipette to remove the fumes of the acid. It is, however, very difficult to absorb the last traces of acetylene by this method.

Oxygen is now absorbed with alkaline pyrogallol. Phosphorus cannot be used for this purpose since even small quantities of acetylene so strongly influence the absorption of oxygen with phosphorus that it is impossible to obtain even approximately correct results for oxygen under these conditions.

The remainder of the gas is now passed into an ammoniacal cuprous chloride solution to absorb the last trace of acetylene. The methane and hydrogen still remaining are determined by combustion.

If only an oxygen determination is to be made, a small quantity of alkaline pyrogallol is drawn into the mercury pipette (Fig. 37), and this reagent is then saturated with the acetylene gas by bringing into the pipette about 100 ccm. of the gas and shaking. The oxygen in an accurately measured sample is then determined by absorption in the usual manner. This mode of procedure is necessary because acetylene belongs to those gases which are quite soluble in water.

The method of analysis first described is, however, to be preferred because the chief part of the acetylene is there first absorbed with fuming sulphuric acid, and the error which might result from the solubility of acetylene in the absorbent is then minimised.

It is always possible that acetylene gas may contain some phosphine, and since this substance is spontaneously inflammable, its determination is of peculiar interest and importance. Lunge has proposed to lead the gas through a solution of sodium hypochlorite and then gravimetrically determine the phosphoric acid which is formed. Bergé and Reychler[1] propose passing the acetylene through nitric acid which contains small amounts of metallic salts, or of leading it into an acid solution of mercuric chloride. These authors found in 1 cm. of acetylene (at 0°) 945 to 985 ccm. of phosphine and 1032 to 1417 ccm. of hydrogen sulphide.

A very good method for the determination of phosphine, hydrogen sulphide, and silicon hydride in the presence of one another consists in burning the gas mixture in the apparatus on p. 306, Fig. 92, and then gravimetrically determining the resulting phosphoric acid, sulphuric acid, and silica.

There is no doubt that these methods give quite accurate results; but they consume so much time as to make them inferior to a volumetric method which will permit of the separation of acetylene from phosphine and will enable one to carry out an analysis in a few minutes. For this reason, the author, with the aid of L. Kahl, experimented with a number of solutions which gave promise of affording a method of separation of phosphine from acetylene. A considerable volume of phosphine was first prepared by heating an alcoholic solution of potassium hydroxide, to which white phosphorus had been added. The gas was collected and kept over water in a glass gasometer. It contained a considerable amount of hydrogen and a small amount of air. The results given below cannot, therefore, lay claim to complete scientific accuracy. The acetylene used in the experiments was prepared fresh each time in an apparatus similar in construction to the Döbereiner lamp.

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[1] *Bull. Soc. Chim.* [3], **17**, 218.

In bringing the gases into contact with the different reagents, 1 ccm. of the reagent was first drawn into the pipette filled with mercury, 100 ccm. of the gas was then introduced, and the pipette was shaken for three minutes. The portion of the gas not then absorbed was transferred to a gas burette and measured. If the reagent acted upon mercury it was placed in a small bulb absorption apparatus, and this was connected with a mercury gas pipette on the one side and with a gas burette on the other, and the absorption was brought about by passing the gas mixture backward and forward through the liquid for three minutes.

The results given in the following table show the number of cubic centimeters of gas which 1 ccm. of the reagent in question was able to absorb under the above conditions.

Reagent employed	Cubic centimeters of phosphine absorbed	Cubic centimeters of acetylene absorbed
I. 1 ccm. of hydrochloric acid cuprous chloride made by Winkler's method, p. 203	39.8	9.4
II. 1 ccm. of hydrochloric acid cupric chloride prepared by dissolving 10 grams of crystallised cupric chloride $CuCl_2 \cdot 2\ H_2O$ in 100 ccm. of water and adding 5 ccm. of concentrated hydrochloric acid	8.6	5.2
III. 1 ccm. of a sulphuric acid copper sulphate solution prepared by dissolving 15.6 g. crystallised copper sulphate $CuSO_4 \cdot 5\ H_2O$ in 100 ccm. of water and adding 5 ccm. of dilute sulphuric acid (1 : 4 by volume) .	8.8	0.2
IV. 1 ccm. of sodium hypochlorite prepared by dissolving 10 g. of crystallised sodium carbonate in 100 ccm. of water, adding an excess of bleaching powder and filtering .	3.0	0.6
V. 1 ccm. of sodium hypobromite prepared by dissolving 100 g. of caustic soda in 1250 ccm. of water and adding 25 g. of bromine . . .	Explosion occurred when this reagent came in contact with the gas mixture.	
VI. The same solution as under V but diluted with 4 times its volume of water	. . .	. 1.3
VII. Sodium hypochlorite prepared by passing chlorine into a solution of sodium hydroxide. This solution was brought to the same strength and the same degree of alkalinity as solution V by the addition of sodium hydroxide and water. Its strength was determined with Penot's solution and its alkalinity with normal sulphuric acid . . .	. . .	0.7

Reagent employed	**Cubic centimeters of phosphine absorbed**	**Cubic centimeters of acetylene absorbed**
VIII. Potassium permanganate, 5 per cent solution	3.2	2.6
1.25 per cent solution . . .	1.0	1.2
IX. Silver nitrate, 3 per cent solution	. . .	1.6
X. Nitric acid solution of copper sulphate prepared by dissolving 78 g. of copper sulphate $CuSO_4 \cdot 5\,H_2O$ in a mixture of 250 ccm. of concentrated nitric acid and 250 ccm. of water	1.2	0.8

The above results show that of the solutions which were examined the sulphuric acid solution of copper sulphate is the best absorbent for the separation of phosphine and acetylene.

Many attempts were then made to carry out this method of absorption in gas pipettes, but it was soon found that the action of light had great influence upon the results. In attempting to saturate a sulphuric acid solution of copper sulphate with acetylene gas, the reagent being contained in a double gas pipette, it was found that even in diffused daylight the copper solution took up further amounts of acetylene upon standing. The same result was obtained with sodium hypochlorite. Careful study of this reaction showed further that the behaviour of acetylene gas when brought into contact with copper sulphate alone is very different from its behaviour when brought into contact with copper sulphate and metallic mercury in the presence of phosphine. We have found that when mercury and an excess of copper sulphate are present the diminution in volume which should result from the absorption of the phosphine in the acetylene gas corresponds exactly to four times the volume of the phosphine present.

Experiments were next made to ascertain whether acetylene which is free from phosphine behaves differently when brought into contact with copper sulphate alone or with copper sulphate and mercury. Acetylene which had been completely freed from all phosphine by treatment with copper sulphate was passed into a small bulb apparatus containing copper sulphate and into another apparatus containing copper sulphate and mercury. The measurement showed that 2 ccm. of an acid copper sulphate solution absorbed exactly the same amount, 0.4 ccm., of acetylene in each case.

The experiments with mixtures of acetylene and phosphine were complicated by the fact that phosphine when exposed to the light and in contact with water containing air decomposes with the separation of phosphorus and the formation of water, a behaviour which renders it extremely difficult to prepare mixtures of the two gases of accurately known composition.

The results given below were obtained by mixing carefully measured amounts of acetylene and phosphine in a gas burette filled with mercury. The phosphine was prepared in the manner above described.

Direct absorption with bromine water in an absorption pipette showed a diminution in volume of 25.8 ccm. when the reagent acted upon a mixture of 50.4 ccm. of nitrogen and 48.2 ccm. of phosphine.

A second treatment of this gas residue with the same absorbent gave no further diminution in volume. The purity of the phosphine was thus ascertained to be 53.5 per cent.

A mixture of 94 ccm. of nitrogen and 2 ccm. of this phosphine gave upon absorption with copper sulphate solution a diminution of 1 ccm. corresponding to 50 per cent of phosphine in that gas.

A mixture of 91.8 ccm. of nitrogen and 2.2 ccm. of phosphine gas and copper sulphate gave a diminution of 1.1 ccm. corresponding to 50 per cent.

A mixture of 94 ccm. of nitrogen and 5.2 ccm. of phosphine gave 3 ccm. corresponding to 57.6 per cent.

A mixture of 91.6 ccm. of nitrogen and 5.2 ccm. of phosphine gave 3 ccm. corresponding to 57.1 per cent.

A mixture of 94.3 ccm. of nitrogen and 2.9 ccm. of phosphine gave 1.5 ccm. corresponding to 51.7 per cent.

All experiments were carried out with the greatest care. The variation in the results is to be explained by the decomposition of the phosphine by the oxygen dissolved in the water and by the action of light. Since it is necessary to keep the containing vessels moist in order to exclude errors resulting from the tension of aqueous vapour, it is impossible to avoid the above error even when working with apparatus filled with mercury. The following values show, nevertheless, that an acid copper sulphate solution in an apparatus filled with mercury is a very good absorbent for the removal of phosphine from acetylene gas.

The mean value obtained for the purity of the phosphorus employed was 52.4 per cent.

Mixtures of acetylene and phosphine when shaken with mercury and 3 ccm. of an acid copper sulphate solution which had previously been saturated with acetylene gave the results tabulated below. The copper sulphate solution was prepared as described under Experiment III on p. 316.

Another cause for a lack of uniformity in the results is to be found in the difficulty of keeping the reagent saturated always to the same degree with acetylene gas.

To determine the phosphine in a sample of acetylene gas, measure off the gas in a gas burette filled with mercury, and then pass the sample over into a gas pipette filled with mercury and containing 3 ccm. of an acid copper sulphate solution which has been prepared as above described and which has been previously saturated with acetylene by shaking it with a sufficient amount of this gas. Shake the gas mixture with the reagent for three minutes and then measure the remaining volume. The fourth part of the diminution in volume thus found represents the volume of phosphine present.

Volume of Acetylene Gas Used	Volume of 52.4 per cent Phosphine Used	Volume of Phosphine Present	Observed Diminution in Volume	Volume of Phosphine found in the Experiment, assuming that it corresponds to one-fourth of the observed diminution in Volume
92.8	5.6	2.90	11.2	2.80
90.2	7.4	3.90	13.4	3.40
94.6	2.4	1.20	4.6	1.15
92.2	5.2	2.70	10.6	2.65
94.0	3.2	1.67	8.3	2.0
82.	5.4	2.82	11.0	2.75

A large number of analysts have found that acetylene gas contains sulphur; but since the gas is evolved from a strongly alkaline liquid, it is probable that the sulphur which is present is chiefly in the form of organic sulphur compounds and is not present as hydrogen sulphide.

CHAPTER IV

GASES WHICH OCCUR IN THE MANUFACTURE OF SULPHURIC ACID

In the manufacture of sulphuric acid the gases which engage the attention of the analyst are: —

1. Sulphur dioxide; it may also be desired here to determine at the same time the small amount of sulphur trioxide present.
2. Nitrous oxide.
3. Nitric oxide.
4. Nitrogen trioxide.
5. Nitrogen peroxide.
6. Oxygen.

The examination of the gas mixture for nitrous oxide and nitrogen peroxide is very rarely desired.

1. *Sulphur Dioxide*

In the manufacture of sulphuric acid the determination of the sulphur dioxide in the kiln-gases is of especial importance. Reich's method[1] has been universally adopted for this purpose. Reich's apparatus consists of a double-necked absorption bottle *A*, the aspirator *B*, and the glass cylinder *E*.

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[1] F. Reich, *Berg- und Hüttenmänn, Zeitung*, 1858; also Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II, pp. 118 and 353.

These are supported by a wooden stand, as shown in Fig. 95. The rubber tube joining *A* and *B* is about 30 cm. long. *A* is half filled with water, and 10 or 20 ccm. of a $\frac{1}{10}$ normal iodine solution are added. The aspirator *B* is filled with water.

Before making a determination, the air in the tubes leading to the apparatus is displaced by the gas to be examined. The apparatus is tight if, after a short time and as soon as the air in *A* is correspondingly expanded, the water ceases entirely to flow from the aspirator.

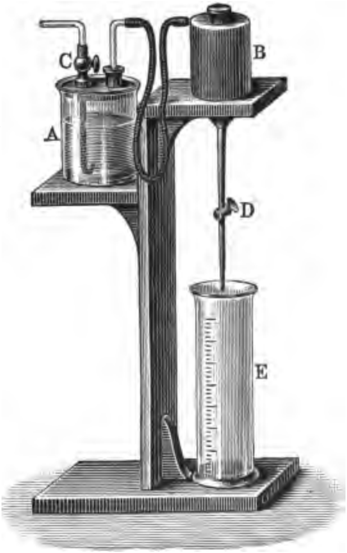

FIG. 95.

In making a determination the stopcock *C* is opened, and the amount of water which is necessary to draw over sufficient gas to decolour the iodine solution is measured in the cylinder *E*. During the experiment the bottle *A* is shaken. The volume of the water which has run out is equal to that of the gas taken, less the volume of the sulphur dioxide absorbed in *A*, and the quantity of sulphur dioxide present can be told from the amount of iodine used. Hence the per cent of sulphur dioxide present can be easily calculated. In accurate work the variations of temperature and pressure must of course be taken into account.

When 10 ccm. of $\frac{1}{10}$ normal iodine solution are used all calculation may be avoided by using the following table, given by Lunge in his book on the Soda Manufacture: —

Water from Aspirator ccm.	Volume per cent of SO_2 in the Gas
82	12.0
86	11.5
90	11.0
95	10.5
100	10.0
106	9.5
113	9.0
120	8.5
128	8.0
138	7.5
148	7.0
160	6.5
175	6.0
192	5.5
212	5.0

Provided that 6 per cent by volume of oxygen is present in the kiln-gases when they leave the lead-chamber, the gases should contain, according to Gerstenhöfer,[1] 10.65 per cent of sulphur dioxide when sulphur is burned, and 8.8 per cent when pyrites is roasted.

If considerable amounts of nitric oxide, nitrogen trioxide, nitrogen peroxide, or nitric acid are mixed with the gases containing the sulphur dioxide, the iodine method cannot be used, and it is best to determine the sulphur dioxide gravimetrically.

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[1] Robert Hasenclever in A. W. Hofmann's *Bericht über d. Entwickelung d. chem. Industrie*, Part I, p. 170.

To determine sulphur trioxide in the presence of sulphur dioxide, the mixture of the two gases is led through a standardised solution of iodine;[1] the amount of the iodine acted upon by the sulphur dioxide is determined with sodium arsenite, and after acidifying with hydrochloric acid, the sulphuric acid is precipitated by barium chloride. Lunge and Salathe have shown that it is difficult to hold back sulphur trioxide with ordinary absorption apparatus. They have used with success the arrangement shown in Fig. 96. *A* is an ordinary bottle. The exit tube *b* is filled with glass beads, and at the lower end it is blown out to a bulb which is pierced with holes. The gas to be examined enters through *a*, passes through the liquid and then through the tube *b*. By sliding the tube *b* up and down, a position may easily be found in which the gas will carry along with it small amounts of the absorbing liquid, and will thus keep the glass beads constantly moistened with the reagent.

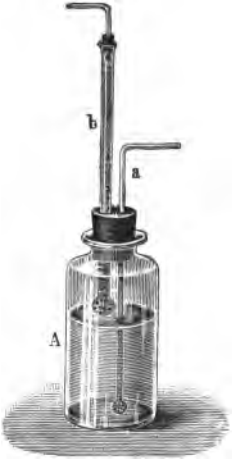

FIG. 96.

Lunge and Salathe used three such wash-bottles in determining the sulphur trioxide in kiln-gases.

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[1] G. Lunge and F. Salathe, *Berichte der deutschen chemischen Gesellschaft*, 1877, 1824.

2. *Nitrous Oxide*

Up to the present time nitrous oxide has not been detected with certainty in the gases of a sulphuric acid manufactory. It is, however, quite probable that this gas may be formed. Very small amounts cannot be determined, but when the quantity rises to about 0.3 per cent it can be determined by burning it with hydrogen in the explosion pipette, after all the absorbable gases have been removed. It must not be forgotten that nitrous oxide is very soluble in water, and that for this reason the absorbents must be carefully saturated with those gases which they do not absorb.

3. *Nitric Oxide*

Nitric oxide may occur in irregular working of the lead-chamber.

For determining the nitric oxide in chamber-gases, Cl. Winkler has proposed[1] that the gases be led first through a concentrated solution of potassium hydroxide, and then, with addition of air, through two small absorption cylinders containing concentrated sulphuric acid. The amount of the nitrogen trioxide thus formed is determined by titration with potassium permanganate, or by decomposition in the nitrometer. At least from 3 to 5 liters should be taken.

4. *Nitrogen Trioxide*

Cl. Winkler has determined[2] the nitrogen trioxide in chamber gases by leading them through 2 to 5 ccm.

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II, p. 314.

[2] *Ibid.*, p. 304.

of $\frac{N}{100}$ potassium permanganate, which had been previously acidified with sulphuric acid, and had also been somewhat diluted, until the permanganate solution was decoloured. The per cent can then be calculated from the amount of water which has flowed from the aspirator, as is done in Reich's method.

Agreeing results were obtained by the above method when the nitric acid was first absorbed by concentrated sulphuric acid, and was then titrated with $\frac{N}{10}$ potassium permanganate.

5. *Nitrogen Peroxide*

In the manufacture of sulphuric acid the nitrogen peroxide which comes in question is always accompanied by nitrogen trioxide. According to Winkler and Lunge the nitrogen peroxide can be best determined by first absorbing the nitrogen peroxide and nitrogen trioxide together by concentrated sulphuric acid. A portion of the solution thus obtained is titrated with $\frac{N}{10}$ potassium permanganate, and in the other portion the gases are determined as nitric oxide in the nitrometer.

6. *Oxygen*

To determine the per cent of oxygen in the chamber-gases, all of the acid constituents are first removed by absorption with potassium hydroxide, and the oxygen is then absorbed with phosphorus as suggested by Lindemann.

CHAPTER V

ANALYSIS OF THE GASES EVOLVED IN THE ELECTROLYSIS OF CHLORIDES

In the development of electrolytic processes for the preparation of chlorine and caustic alkalies the analysis of the gases which are evolved furnishes a method of control over the process and is therefore of first importance. The gases coming from the anode will contain, in addition to free chlorine, both oxygen and carbon dioxide, and in the mercury processes hydrogen may also appear. The current yield is the better the higher the percentage of chlorine in the gases and the lower the amount of oxygen and carbon dioxide.

Analytical results of sufficient accuracy for practical purposes are obtained by drawing the gases into a simple gas burette filled with water, reading at once the gas volume thus drawn off, and then, with the aid of a small 5 ccm. pipette, introducing into the burette through the rubber tube at its top a 50 per cent solution of potassium iodide. Upon shaking the gas with this reagent all chlorine is at once absorbed while carbon dioxide, oxygen, hydrogen, and nitrogen remain behind. The gas is then passed into a potassium hydroxide pipette to absorb the carbon dioxide and is transferred to a pipette for solid and liquid reagents (see p. 52) containing metallic copper, ammonia, and ammonium carbonate solution. These will absorb the oxygen. Hydrogen is determined by combustion, using one of the methods described in Part II, Chapter III, pp. 130 to 143.

Gases which are evolved under other conditions, especially in electrolytic processes that are carried on without diaphragms, consist chiefly of hydrogen and oxygen. The oxygen in such a mixture may best be absorbed with the copper pipette mentioned above. The use of phosphorus is dangerous because of the occasional occurrence of an explosion.

CHAPTER VI

DETERMINATION OF THE GASES WHICH OCCUR IN THE MANUFACTURE OF BLEACHING POWDER

1. *Determination of the Amount of Chlorine in the Chamber-air*

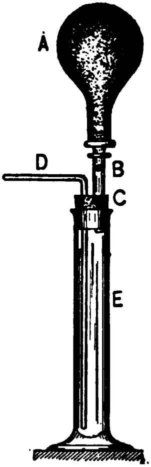

Fig. 97.

The determination of chlorine in chamber-air is accomplished by the use of a solution of potassium iodide and sodium arsenite, with the addition of calcium carbonate.[1] The apparatus which is employed is shown in Fig. 97. It consists of a glass cylinder *E* provided with a two-hole rubber stopper, through one opening of which is inserted the glass tube *D* passing nearly to the bottom of the cylinder. The outer end of *D* must be drawn out to an opening no larger than a small needle. Through the other opening of the stopper there is inserted a short tube *B*, which has a small opening in the side, and to the upper end of this tube is attached a rubber bulb of about 100 ccm. capacity. There is first placed in *E* 26 ccm. of the iodide-arsenite solution, to which has been added a little starch paste. The solution is prepared by dissolving 0.3485 g. of arsenious acid in sodium carbonate, and neutralising this with sulphuric acid, then adding 25 g. of potassium iodide, 5 g. of precipitated calcium carbonate, and 6 to 10 drops of ammonia, the whole being finally diluted to 1 liter with water. The outer end of *D* is inserted into an opening in the side of the chamber, about two feet from the bottom. The bulb *A* is then tightly compressed with the hand, the hole in the side of *B* is closed with the finger, and the pressure on *A* is released. The expansion of the bulb draws the chamber-air from *D* and through the liquid in *E*. The operation is continued until the liquid in the cylinder shows a colour, the number of compressions of *A* being noted. If the capacity of the bulb is about 100 ccm. ($\frac{1}{250}$ cubic foot), then the appearance of colour with 10 aspirations indicates 2½ gr. of chlorine per cubic foot, or 5 gr. with 5 aspirations.

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[1] Lunge, *Sulphuric Acid and Alkali*, 2d ed., **3**, 458.

The chlorine can also be determined by drawing it through absorption bottles containing an aqueous solution of potassium iodide, and titrating the liberated iodine with $\frac{N}{10}$ arsenious acid.

2. *Determination of Chlorine in the Presence of Hydrochloric Acid Gas*[1]

These gases occur together in the mixture coming from the decomposers of the Deacon process. 5 liters of the gas mixture is drawn through 3 gas wash-bottles, which together contain 250 ccm. of a solution of sodium hydroxide, whose specific gravity is 1.076. After the gas has been passed through these bottles, the liquid in the three is united and diluted to 500 ccm. 100 ccm. of this solution is then placed in a flask fitted with a Bunsen valve, and an excess of a solution of ferrous sulphate[1] is added. The latter is then boiled, diluted with 200 ccm. of water, and titrated back with $\frac{N}{2}$ potassium permanganate. This gives the amount of free chlorine.

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[1] Neumann, *Gas Analyse und Gasvolumetrie*, 1901, p. 146.

To another portion of 10 ccm. of the solution some sulphur dioxide is added, and the liquid is then acidified with sulphuric acid, boiled, cooled, and the free sulphur dioxide destroyed by the addition of potassium permanganate. The solution is now neutralised with sodium carbonate, diluted, and, after addition of potassium dichromate, is titrated with $\frac{N}{10}$ silver nitrate solution. This gives the total chlorine ($Cl + HCl$).

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[1] 100 g. $FeSO_4$ and 100 g. concentrated H_2SO_4 in 1 liter.

CHAPTER VII

THE ANALYSIS OF ATMOSPHERIC AIR

IN the analysis of atmospheric air, the chemist has to deal with the following constituents: —

1. Aqueous vapour.
2. Carbon dioxide.
3. Carbon monoxide.
4. Oxygen.
5. Ozone.
6. Argon.
7. Sulphur dioxide and sulphuric acid.
8. Nitrogen.

For sanitary purposes, the determinations of carbon dioxide and water are those most frequently desired.

1. *The Determination of Aqueous Vapour in the Atmosphere*

The water can be determined with great exactness by leading a measured or weighed volume of air through tubes filled with calcium chloride or phosphorus pentoxide, and ascertaining their increase in weight. It hardly need be mentioned that the calcium chloride must first be treated with carbon dioxide, so that it may contain no basic salt which, by taking up carbon dioxide, could change in weight. The common phosphorus pentoxide is never pure, but always contains traces of phosphorus and phosphorous acid. For this reason, a current of dry air should be led for some time through the absorption apparatus before it is used.

Pettersson has devised an admirable apparatus with which the moisture and carbon dioxide of the atmosphere can be directly determined volumetrically. (See the determination of carbon dioxide in air, p. 346.)

For most purposes the hair hygrometer and the psychrometer give sufficiently accurate results.

A very fine form of the hair hygrometer devised by Saussure is made by Hermann Pfister, in Berne.

The construction of the instrument is based upon the property possessed by hair from which the oil has been removed, of lengthening or shortening according to the amount of moisture in the air. By alternately moistening and drying the hair thoroughly for a number of times, it is given, according to Pfister, the property of quite regular expansion.

Figure 98 shows the arrangement. A hair, prepared as above mentioned, is fastened to a suitable frame. The hair passes around a little wheel below, and the changes in length cause the pointer to move and give the relative moisture directly on the scale.

August's psychrometer is based on the fact that water exposed to the air evaporates the more rapidly, and thereby extracts more heat from its surroundings, the farther the air is removed from the condition of saturation. From the lowering of the temperature $(t - t^1)$ of a thermometer which has been moist-

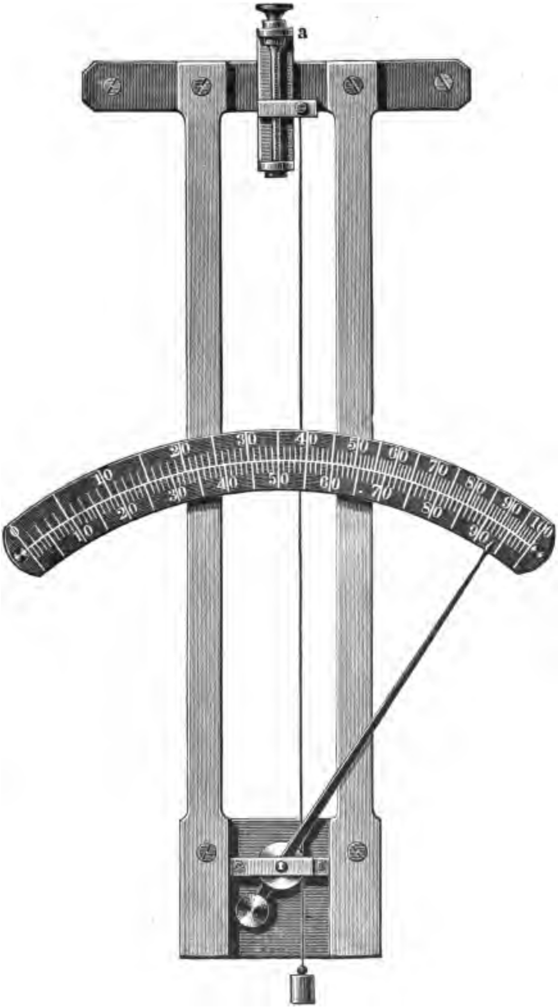
a
10
20
30
40
50
60
70
80
90
100
10
20
30
40
50
60
70
80
90

FIG. 98.

ened in a suitable manner, the tension e of the water vapour in the air is calculated from the formula —

$$e = e^1 - k\ (t - t^1)\ b,$$

in which e^1 is the tension corresponding to the temperature t^1, b the barometric pressure in millimeters, and k an empirical factor which has, according to the researches of Regnault, the following values: —

In small closed rooms	0.00128
" large "	0.00100
" halls with open windows	0.00077
" courts	0.00074
" open air (no wind)	0.00090

2. *The Determination of Carbon Dioxide in the Atmosphere*

The most varied experience has shown that through the process of breathing the air acquires properties which cause it to act deleteriously upon health when the products of breathing exceed a certain limit. Since we are not able by ordinary means to determine the other substances which are here formed, we make use of Pettenkofer's suggestion and judge of the purity of the air by the per cent of carbon dioxide present.

According to Pettenkofer, the carbon dioxide in the air should not be raised, by breathing, to over 0.1 per cent.

The process best suited to the quantitative determination is that first used by Saussure and modified by Pettenkofer: it consists in absorbing the carbon dioxide of a measured volume of air with a barium hydroxide solution of known strength, and then determining, by titration with oxalic acid, the amount of barium hydroxide still unacted upon. This method has been used by many investigators, and has been modified in minor details. A very practical form is that devised by W. Hesse.

Clemens Winkler[1] describes the method as follows: —

"W. HESSE'S METHOD.[2]—This method is superior to the method of Pettenkofer, upon which it is based, in that it simplifies and shortens the determination of carbon dioxide, and can also be carried out at the place where the sample is taken, the possibility of employing it being thus much greater than formerly. By lessening the volume of the air to be examined, it became possible to diminish the size of the apparatus to portable form without limiting thereby the number of determinations.

"The necessary apparatus may be divided into a stationary and a portable portion.

"*A*. The reserve apparatus in the laboratory comprises the following: —

"1. A glass balloon or large bottle holding several liters, and filled with a concentrated solution of barium hydroxide. 1 kg. of barium hydroxide and 50 g. of barium chloride are put into from 4 to 5 kg. of distilled water. As the solution is used it is replaced by water as long as there is material in excess to saturate the water.

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[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II, p. 375.

[2] Dr. W. Hesse, *Anleitung zur Bestimmung der Kohlensäure in der Luft, nebst einer Beschreibung des hierzu nöthigen Apparates;* Eulenberg's *Vierteljahrsschr. f. gerichtl. Medicin und öffentl. Sanitätswesen*, N.F. xxxi. 2.

"2. A bottle containing dilute baryta water. The bottle is provided with a small absorption flask containing pumice-stone saturated with caustic potash, for freeing the entering air from carbon dioxide (Fig. 99). This dilute baryta water is made by adding about 30 ccm. of concentrated barium hydroxide solution to 1 liter of water, or directly by dissolving 1.7 g. of a mixture of barium hydroxide and barium chloride (20 : 1) in 1 liter of distilled water.

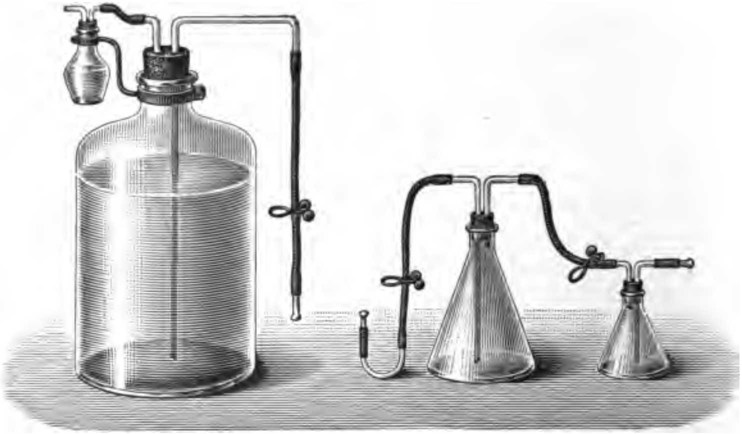

FIG. 99.

"3. A solution of oxalic acid containing 5.6325 g. of crystallised oxalic acid in 1 liter of water. 1 ccm. = 1 ccm. CO_2.

"4. A solution of phenol-phthaleïn, 1 part in 250 parts of alcohol.

"*B.* The portable apparatus comprises—

"1. Five thick-walled conical Erlenmayer flasks of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{12}$, and $\frac{1}{16}$ liter capacity, and supplied with well-fitting, double-bore rubber stoppers. The point to which the rubber stopper reaches is marked on the first four flasks, and their capacity up to this mark is written on the outside of each flask with a diamond. The openings of the stoppers of these four flasks are closed with pieces of glass rod from 3 to 5 cm. long. These rods are well rounded at the lower ends, the upper ends being widened like a button.

"2. A thick-walled 10 ccm. pipette.

"3. A glass stopcock burette holding from 10 to 15 ccm., graduated in tenths, and having a tip 7 to 10 ccm. long.

"4. A 300 ccm. flask provided with a small guard bottle, as in *A* 2, and filled with dilute baryta water. This is filled in the laboratory by connecting it with the large reserve bottle containing dilute baryta water, and driving the solution over through the siphon. Before beginning the experiment a few drops of a solution of rosolic acid are added to the barium hydroxide solution. The fainter the colour the sharper is the reaction, but the colour must not be so faint as to be indistinct. The proper coloration will last for about three days; it is then so indistinct that a few drops of rosolic acid must again be added.

"5. A 250 ccm. bottle filled with dilute oxalic acid. This is prepared by bringing 25 ccm. of the standardised oxalic acid into the 250 ccm. flask, and then filling the flask to the mark with water.

"6. A thermometer.

"7. A barometer (a small aneroid).

"The amounts of solutions here given for the portable apparatus are sufficient for thirty separate determinations; in other words, at least ten analyses, including a control determination each time and the standardising of the solution, can be made with the above quantities.

"Each determination of carbon dioxide by Hesse's method is a double one, the two determinations being made with volumes of air of different size. Accordingly, flasks of $\frac{1}{2}$ and $\frac{1}{4}$, or $\frac{1}{4}$ and $\frac{1}{8}$, or $\frac{1}{4}$ and $\frac{1}{12}$ liter capacity are used for taking the samples of air, the sizes of the flasks chosen depending upon whether a smaller or a larger amount of carbon dioxide in the air is to be expected. The samples are taken by completely filling the flasks at the place where the air is to be examined with water which has the temperature of the place, and then emptying the flasks and rinsing them with distilled water. In this operation care must be taken that the flask is not warmed by the hand, and that no air exhaled by the operator enters the flask.

"To absorb the carbon dioxide, the 10 ccm. pipette is put through one of the openings of a stopper fitting the flask, its end is inserted in the rubber tube of the supply flask, and the pipette is rinsed with a little barium hydroxide solution drawn up into it. The pipette is now filled to the zero mark by suction, and the stopper through which it passes is inserted in the neck of the flask containing the sample of air. The barium hydroxide is now run into the flask, the second opening of the stopper being obstructed with the finger or a glass rod to such an extent that the displaced air can just escape. The glass rod is then pushed into place, and the pipette is freed from the few drops of solution adhering to it by closing it at the top and warming it with the hand. The pipette is then drawn out of the stopper, and the second opening is closed with a glass rod. The same proceeding is repeated with a second flask of different capacity. The two flasks are allowed to stand for some time with occasional shaking, and in the meantime the strength of the baryta water is determined.

"The strength of the baryta water is determined by putting into the small flask of $\frac{1}{16}$ liter capacity nearly as much standardised oxalic acid solution as will be required in the titration, and then running in 10 ccm. of the solution of barium hydroxide. The solution is then neutralised by slowly running in more oxalic acid, and the total oxalic acid necessary is thus determined. By proceeding in this manner a very exact standardising of the solution is possible, even in an atmosphere containing much carbon dioxide, because the solution is never strongly alkaline enough to absorb appreciable amounts of carbon dioxide from the air.

"The baryta water which has been shaken with the air is titrated without previously removing the barium carbonate. The titration is made as follows: —

"Remove the glass rod from one of the openings in the stopper, and immediately insert the tip of the burette which has already been filled with oxalic acid solution. The tip of the burette should reach as far as possible into the flask (Fig. 100). Open the stopcock of the burette and allow the oxalic acid to enter rapidly at first, but at the last only drop by drop. If the increased pressure resulting inside the flask checks the flow of liquid from the burette, this pressure is removed by lifting the glass stopper for a moment. When the solution is neutral, *i.e.* when it is completely decoloured, the height of the solution in the burette is noted, and the contents of the second flask is titrated in the same manner.

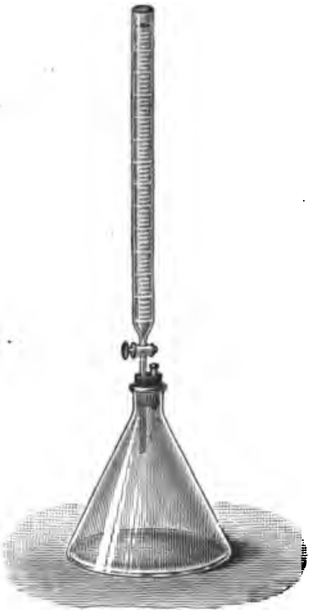

Fig. 100.

"It is clear that when the amount of carbon dioxide present is small, the accuracy of the determination is increased by using larger volumes of air. For this reason Hesse uses a flask of ¾ or 1 liter capacity whenever the carbon dioxide is probably below the limit for dwelling-rooms, as, for example, in the open air. He also uses three sizes when great accuracy is desired. Of course sufficient barium hydroxide solution must be taken to insure its being present in excess up to the end of the operation. The small amount of carbon dioxide which the baryta water takes up from the air that it displaces when running into the flask may be disregarded.

"In using this method for determining the carbon dioxide present in the soil or in walls, Hesse employs the apparatus shown in Fig. 101. The air in the soil is drawn through the flask by means of a rubber pump; the glass tubes are then removed, and the openings in the stopper are closed with glass rods. The titration is made as before described, but more concentrated reagents are required. In examining the air of graves, Hesse used a solution of barium hydroxide ten times as strong as that previously given (10 ccm. = about 10 ccm. oxalic acid solution A3 = 10 ccm. CO_2).

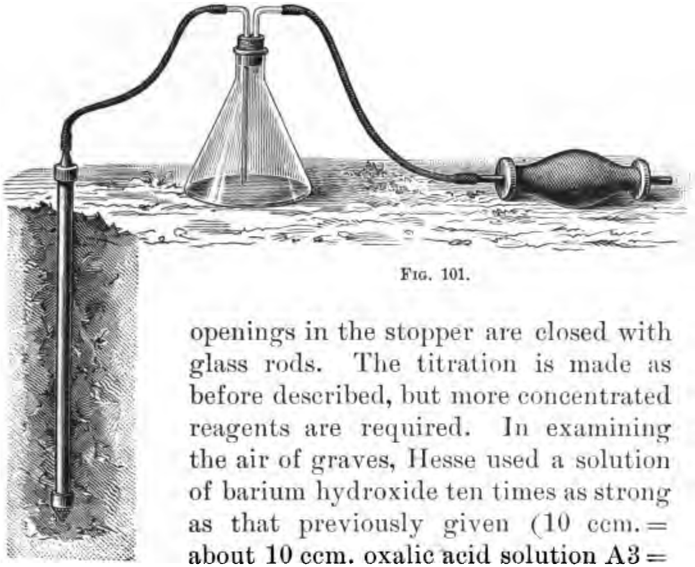

FIG. 101.

"In calculating the analysis, the volume of air taken is reduced to normal pressure and temperature so that correct comparisons may be made. This calculation takes considerable time, and to Hesse belongs the merit of having compiled a table[1] giving the figures by which the amounts of carbon dioxide found in the uncorrected gas volume are to be multiplied. The table contains for each degree of temperature the multiplier for any barometric pressure.

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[1] Dr. med. Walter Hesse, *Tabellen zur Reduction eines Gasvolumes auf* 0° *Temperatur und* 760 *mm. Luftdruck.* Braunschweig, 1879.

"Example —

$$V = 223 \text{ ccm.}, t = 19°, b = 739 \text{ mm.};$$

the titration of the baryta water gave 10 ccm. baryta water = 11.5 ccm. oxalic acid, and in the experiment 6.2 ccm. oxalic acid was used. Hence the amount of carbon dioxide which had already united with the barium hydroxide was equivalent to 11.5 – 6.2 = 5.3 ccm. oxalic acid, corresponding to 0.53 ccm. CO_2, and we have the proportion —

$$[223 - 10]^{1} \text{ or } 213 : 0.53 = 1000 : x,$$

$$x = 2.49 \text{ ccm. (in unreduced liter).}$$

"The multiplier corresponding to this temperature and barometric pressure is 1.100; hence in the reduced liter there are 2.49 × 1.100 = 2.7 ccm. or in the air examined 2.7 parts per thousand of CO_2 present.

"The whole operation, including the control determination and the calculation, may be completed in from a quarter to half an hour. Hesse recommends that the results be put down in the form shown in the following table. The examples given show how well the results agree even under the most varied modifications. The calculations of the results given

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[1] Subtraction from the volume to allow for the barium hydroxide solution which was run in.

Date	Place	Building	Floor	Number of persons in the room	*h*	*t*	*b*	V	BW	Titer	Oxal.	CO_2 unreduced	Multiplier	CO_2 reduced	Remarks
18.12.'78	Schwarzenberg	School	1st	68	3 P.M.	22	710.5	984	40	27.100	28.00	8.6	1.156	9.9	After a two-hour session
								787	35		29.40	8.7		10.1	
								556	30		36.00	8.6		10.0	
								261	15		19.40	8.6		10.0	
								136	15		30.30	8.9		9.9	
4. 1.'79	"	Bath	2d	3	8.30 P.M.	17	716.0	556	15	9.300	3.75	1.9	1.128	2.2	
								261	15		8.70	2.1		2.4	
								136	15		11.50	2.0		2.3	
5. 1.'79	"	Outside atmosphere		...	12 M.	?	722.0	984	15	9.300	11.30	0.27	1.134	0.3	Titrated in a room at 21°
								261	15		13.30	0.26		0.3	
19. 1.'79	"	Bath	2d	1	8 A.M.	17	732.0	984	10	9.350	4.10	0.5	1.103	0.6	
								556	10		6.20	0.6		0.6	
								136	10		8.65	0.6		0.6	
27. 6.'79	Schneeberg	Apothecary's store	1st	2	2.45 P.M.	19	726.0	611	10	11.675	6.90	0.8	1.120	0.9	
								279	10		9.60	0.8		0.9	

in the table[1] were made with the aid of logarithms, but are carried out to only one decimal."

PETTERSSON'S METHOD

A very exact method for the determination of carbon dioxide and water vapour has been devised by Pettersson.[2] He describes the method as follows: —

"With the apparatus shown in Fig. 102 an accurate determination of the water and carbon dioxide in the air may be quickly made.

"*A* is a pipette with a graduated tube. It is joined at the top, by narrow but not capillary glass tubes, to the two reservoirs *B* and *C*. *B* is loosely filled with glass-wool and phosphorus pentoxide, and *C* with glass-wool and soda-lime. For the sake of clearness the connecting tubes are drawn in the figure much wider than they really are. The remainder of the apparatus, however, is shown so far as possible in the proper proportions. The whole system of the three glass reservoirs is immersed in a vessel of

---

[1] In the table —
h = time of day.
t = temperature centigrade.
b = barometric pressure in millimeters of mercury.
V = volume of glass flask.
BW = cubic centimeters of baryta water used.
Titer 9.35 means that 10 ccm. barium hydroxide solution = 9.35 ccm. oxalic acid = 0.935 ccm. CO_2.
Oxal. = cubic centimeters of oxalic acid solution used.
CO_2 unreduced = carbon dioxide in cubic centimeters in the unreduced liter.
CO_2 reduced = carbon dioxide in the reduced liter = parts per thousand.

[2] *Zeitschrift für analytische Chemie*, 25, 467–484.

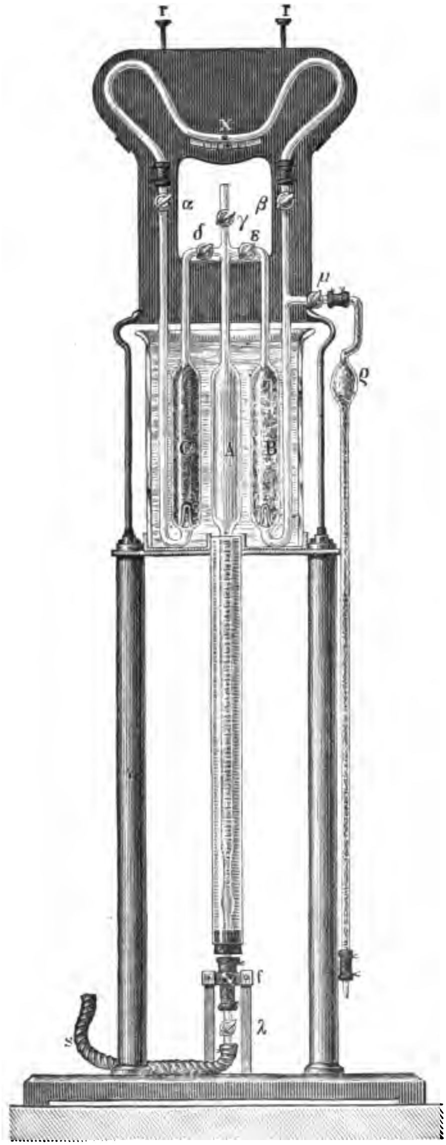

FIG. 102.

water in which the temperature is kept uniform, but of course not constant, by means of a stirrer. The handles of the stirrer are shown in Fig. 102, *r r*, and the disk in Fig. 103, ***R***.

"The analysis consists in measuring a sample of air in the pipette *A*, then driving it over into the drying cylinder *B*, bringing it back into *A*, and measuring the decrease of volume caused by the drying. Then in similar manner

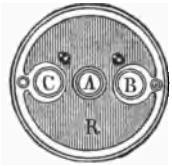

FIG. 103.

the carbon dioxide present in the dried air is absorbed in *C*, and the decrease of volume is measured in *A*. The analysis thus comprises two different kinds of operations —

"1. The driving back and forth of the air from one vessel to another.

"2. The adjusting of the mercury level in the graduated tube, and the measuring of the volume of the air enclosed in *A* after each operation.

"1. The air to be examined is taken directly from the room or from the free atmosphere by means of a glass tube connected with the upper end of the pipette and passing out into the open air. The pipette in the beginning is entirely filled with mercury, and the air is drawn in by allowing this mercury to run out until it stands about at the lower zero mark of the graduated tube. The stopcock λ is then closed, and the level of the mercury is accurately adjusted with the screw *f*, which, by means of a brass plate, compresses the rubber tube joining the stopcock λ with the graduated tube. If the level in the graduated tube has been brought at the beginning to nearly the proper position, a slight turning of the screw suffices for an accurate adjustment of the mercury, The adjustment may be made still sharper by using a magnifying glass. During this operation there is considerable pressure in the rubber tube upon which the screw acts. For this reason a piece of thick-walled rubber tubing is chosen, and, after it has been placed in position, an envelope of strong silk is sewed around it. The rubber will then hold for an unlimited time without bursting.

"When the pipette has been filled with air, δ, ϵ, a, and β are opened so that there may be the same pressure throughout the apparatus, and the stirrer is set in motion so that all parts of the apparatus may take the same temperature. The small drop of liquid x in the differential manometer will then come to rest opposite one of the marks on the little scale. This position must be accurately observed with the magnifier, because in all subsequent operations the drop must be brought to exactly the same position before a reading of the volumes is taken. After one is convinced that all differences of temperature and pressure have been equalised, γ, δ, and β are closed. ϵ is left open. λ is now opened, and the mercury reservoir is raised by means of a sliding arrangement. The pipette *A* gradually fills with mercury, and the air is driven over into *B*. As *B* was full of dry air in the beginning, the pressure in it becomes quite high, and although in my apparatus the volume of *B* is about one-third larger than *A* (which contains exactly 100 ccm.), the movable mercury reservoir must be raised nearly 130 cm. in order to raise the mercury in the pipette from the lower zero mark to the T of the connecting tubes at the top, and thus drive all of the air in *A* over into *B*.

"As is well known, phosphorus pentoxide absorbs the moisture of the air rapidly and completely.[1] On that account it will perhaps be surprising that, according to my experience, the air entering *B* must be left for ten to twenty minutes in contact with the pentoxide in order to remove every trace of moisture. The result may be easily controlled by again passing the dried air into B, and then measuring the decrease in volume resulting from the second absorption. To be sure, the greater part of the moisture is absorbed in a few minutes, but the traces are removed from the air only after it has stood for some time in the drying cylinder *B*. The apparent difference between earlier experiments and my own experience concerning the rapidity with which phosphorus pentoxide completely absorbs moisture finds an easy explanation in the different conditions under which we operated. Up to the present time experimenters have determined the rapidity with which a current of air passing over phosphorus pentoxide will lose the moisture which it contains. In my experiments a volume of air at rest is exposed to the dehydrating action of the pentoxide, and it is natural that a longer time should be necessary for the absorption to become complete.

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[1] See the work of Fresenius in *Zeitschrift f. analyt. Chemie*, **4**, 177; also Dibbits, *ibid.*, **15**, 121.

"The absorption of the carbon dioxide in *C* is carried out in a similar manner. The stopcocks ϵ and a must be closed and δ opened: γ and μ remain closed during the whole analysis. The carbon dioxide is absorbed much more rapidly by the soda-lime than is the aqueous vapour by the phosphorus pentoxide. Ten minutes are usually sufficient for removing the last traces of the carbon dioxide, so that when the operation is repeated no further decrease in volume can be observed in the graduated tube. Since soda-lime loses one molecule of water for every molecule of carbon dioxide which it absorbs, I naturally expected that the air coming from *C* after having been freed from carbon dioxide would contain a slight amount of moisture, and that this moisture would have to be removed by repeated absorption in *B*. To my surprise, however, the air proved to be completely dry after the absorption of carbon dioxide, and although I passed the air into *B* after each determination of carbon dioxide, I was able to detect in only a few experiments a decrease of volume of about 0.003 or 0.004 per cent. This decrease was of course brought into the calculation, but it may have been accidental, since the average uncertainty in this determination of carbon dioxide amounts to about 0.002 per cent. I would here state that I use in *C* soda-lime which has been thoroughly dried and heated, and that the quantity of carbon dioxide which is absorbed in each experiment (especially in the analyses of air from the streets of Stockholm, where the carbon dioxide amounts to only 0.039 to 0.059 per cent) is exceedingly small in comparison with the large amount of absorbent which certainly contains a great deal of lime. I have had the same experience with two different pieces of apparatus, yet I do not mean to assert that every soda-lime (a product which, as is known, is prepared in very different ways) would have the same action, or that the contents of the reservoir *C* in my apparatus will hold back the moisture as completely after several hundred analyses as it does now. It facilitates and shortens the analysis if the sample of air need be dried but once; and since it has turned out, although contrary to my expectation, that the moisture formed in the absorption of the carbon dioxide can be taken up completely by the soda-lime itself, I would advise that some quick-lime be mixed with the soda-lime. A few control experiments will of course best decide as to whether or not we can depend upon the dehydrating action of the soda-lime.

"2. I now come to the second kind of analytical operation, namely, the adjustment and the measuring of the gas volume. The principle of this new method permits the measuring of the volume of air, after each absorption, by a direct reading of the graduated tube without regard for any changes of temperature and pressure which may have taken place during the experiment. Variations in the pressure of the external atmosphere cannot affect the measurements, because the stopcocks γ and μ remain closed during the whole analysis. The temperature of the water surrounding A, B, and C is kept uniform by stirring. To be sure, the temperature changes constantly, but the change is gradual, and the pressure in all three reservoirs, A, B, and C, rises or falls to the same extent. Two of these reservoirs are always in communication with each other; the third is, however, cut off from the others. For example, during the determination of water, A and B communicate through the stopcock ϵ, and of themselves form a distinct system; the air in C is separated from them from the beginning of the experiment by the closed stopcock δ. The operations above described are now carried out with the air in A, the air being passed into B, then brought back in dry condition into A, and the level of the confining mercury so adjusted by the eye that the air in A has approximately its original pressure. Upon now opening the stopcock β, the little index x in the differential manometer moves toward the right or left, according to whether the mercury in the graduated tube stands too low or too high. λ is closed and the screw *f* is turned until *x* has taken precisely the same position which it had at the beginning. It is obvious that the pressure in *A* and *B* is now identical with the pressure prevailing in *C*, because the air in *C*, the stopcock *a* being open, acts upon the left side of the drop of liquid *x*, and the slightest difference in pressure would cause a great displacement of the drop toward one side or the other. The sensitiveness is, in fact, so great that a very slight turning of *f*, which would increase or diminish the volume of air in *A* by 0.002 ccm., moves the index 1 mm. to the right or left. The nature of the drop of liquid *x*, which plays the part of an index, has a great influence upon the size of the deviation. I prefer to use a drop of concentrated sulphuric acid coloured with indigo blue: the drop, in order to be easily movable, occupies only 3 to 4 mm. of the length of the manometer tube. The tube is slightly bent, so that the drop tends of itself to take a position in the middle. The width of the manometer tube has but little influence, provided that it is not too narrow. An index of high-boiling petroleum is even more sensitive than the sulphuric acid. Since the sensitiveness for slight differences of pressure is so great, the stopcocks *β* and *a* must be opened very carefully, to avoid driving the drop out of the manometer tube. It is best never to open both *a* and *β* at once, but to keep one stopcock closed until the level in the graduated tube has been brought into approximately correct adjustment. If the operation is thus carried out an analysis will never be lost.

“It follows from what has been said that the method in reality consists in bringing the sample of air after each operation under exactly the same relations of pressure and temperature as prevail in the second part of the system. For example, there is present in all parts of the apparatus at the beginning of the analysis a temperature t and a pressure p. During the absorption of the water the air in C is at rest and is separated from A and B. Its temperature changes gradually from t to t_1, the pressure from p to p_1. After the absorption of water, the dry air in A (and also that in B) is brought to the same pressure p_1 with the help of the screw f and the index x in the manner already described. The temperature is of course t_1. Hence the determination in the graduated tube of the decrease in volume is made under another pressure and another temperature from those at the beginning. Nevertheless the decrease in volume gives directly and without correction the volume per cent of the moisture in the air, just as though the dried air were measured under constant temperature and constant pressure. It is easy to understand that if the temperature in the water jacket, and consequently in the whole apparatus, were brought back to t, the air would again have the original pressure p without any change whatever being necessary in the adjustment of the index or of the level of the mercury in the graduated tube. The glass vessels A and B on the one hand, and C on the other, as well as the air contained in them, change their volumes in the same proportion. Hence in this method the changes of temperature during the analysis eliminate themselves, and the determinations give directly (due regard being of course given to the table of calibration) the volume per cents of water and carbon dioxide.

"A few remarks may here be in place. The influence of variations of temperature upon the air volumes which are separated from each other — *A* and *B* from *C* in the determination of moisture, and in the carbon dioxide determination *A* and *C* from *B* — is reciprocally compensated by the uniform expansion of the glass vessels and the dry gases. If after the index has been brought to rest the apparatus is left with the stopcocks a and β open and either δ or ϵ closed, the index does not move although the temperature of the water may slowly change several tenths of a degree. Only when the change of temperature amounts to whole degrees is there seen a tendency of the index to move toward the right or left. This is caused by the unequal expansion of the solid phosphorus pentoxide in *B* and the soda-lime in *C*. The expansion of these substances is for the most part self-compensating, but it is never completely so, and the influence of this source of error is manifested, in experiments which last quite long, as a slight uncertainty amounting to some millionths of the total volume. This degree of accuracy has never been attained by any of the earlier methods for determining the moisture of the atmosphere, so that the slight uncertainty mentioned above may be wholly disregarded when the apparatus is used as a hygrometer. In the determination of the atmospheric carbon dioxide, however, it is desirable that this difficulty be removed. The defect in the compensation could be met by allowing some mercury to enter *B* or *C* until the expansion of the air in both was equal. I have not tried this expedient with my apparatus, because the following procedure accomplished the end.

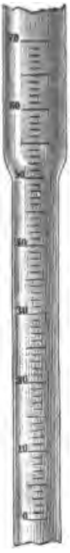

FIG. 104.

"When the volume of the dried air has been measured in *A*, I do not proceed at once to the determination of carbon dioxide in the same volume of air. After the absorption of water the volume of the mercury usually stands in the wider part of the graduated tube (Fig. 104). Instead of making the reading after the carbon dioxide absorption upon the same portion of the scale, where 1 mm. = 0.01116 ccm., I prefer to open the stopcock μ and to allow a small volume of dry atmospheric air to enter *A* through *g* and *B* until the mercury again stands at the lower zero mark of the graduated tube. Since the pipette with the graduated tube holds exactly 100 ccm., it now contains 100 ccm. of dry air under atmospheric pressure. γ, ϵ, a, and β are now opened for a couple of seconds to allow the air in *C* also to assume the pressure of the atmosphere. Then γ, a, ϵ, and μ are closed. δ is left open and the absorption of the carbon dioxide is brought about in ten minutes by driving the air from *A* into *C*. The decrease in volume is then measured in the lower narrow part of the graduated tube where 1 mm. = 0.00199 ccm. In such a short time (the determination of the carbon dioxide does not take half an hour) the temperature will not change enough to make the error in compensation amount to more than about 0.002 per cent. It is best, however, in determinations of atmospheric carbon dioxide which call for great exactness to keep the temperature of the room relatively constant.[1] In analysing the air of rooms, where accuracy to the millionths need not be striven for, the work may be carried on in a newly heated room quite near the stove without any considerable errors resulting. One should, however, seek to avoid the action of direct radiation from a fire or from the sun. For the hygienic examination of the air of rooms, as well as for the hygrometric determination of the moisture of the atmosphere, where the accuracy demanded is not greater than 0.05 per cent, I have a small apparatus in which the pipette *A* holds only 18 ccm., the other parts of the apparatus being correspondingly small. This apparatus can be enclosed in a small wooden box 60 cm. high, and may be carried in the hand. Here also the absorption of the carbon dioxide is made with dry soda-lime, but the absorption of moisture is carried out in an Orsat tube filled with concentrated sulphuric acid. The compensation of the temperature variations is based upon the principle stated below. In this apparatus also the graduated tube has a wide and a narrow portion, but the wider part is *below* and serves for the determination of water, and the carbon dioxide determination is made in the narrow part of the tube which stands *above*.

"In working with the larger apparatus, one finds that the index does not at once come to rest after a determination of water or carbon dioxide has been made, and the mercury in the graduated tube properly adjusted. For from five to ten or twelve minutes the index slowly moves, giving the impression that in the pipette and the absorption vessel communicating with it — either *B* or *C* — the air *is being warmed.* This is actually the case. When the air which has been compressed in *B* or *C* enters *A* it expands *adiabatically* and becomes *cooler.*

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[1] Do not seek to obtain a constant temperature in the apparatus by pouring in warm or cold water. Every such addition is a source of sudden variations of temperature which make themselves known through the oscillations of the index. The index remains quiet only when the apparatus is left to itself.

"Only after several minutes' standing is this loss of heat equalised by the water outside the pipette. On this account the water must be stirred, and the reading must not be made until the index has come to rest. The analysis, which otherwise would take probably less than half an hour, is thus made considerably longer. For this reason, the absorption of water in the small apparatus for hygienic and hygrometric determinations is made in an Orsat tube fused on to the apparatus, the adiabatic cooling being here imperceptible.

"When the water is absorbed by a solid substance it is indispensable that the vessel *B* be previously filled with the *same kind of dry air* as that to be analysed. *A* should not be filled with atmospheric air while *B* contains the dry air of the room, because, for reasons easily seen, the determination of the carbon dioxide would then be inexact. For this reason *B* is filled before the analysis with air of the same nature as that to be analysed later. This air enters *B* through the tube *g* containing phosphorus pentoxide and through the stopcock μ. The air is drawn in by first filling the pipette *A* with mercury, and then, having closed the stopcocks γ, δ, and β, lowering the mercury reservoir. The air enters *B* from below through a small projecting tube over which a U-shaped tube is placed, and takes the place of the air passing from *B* into *A*. The operation must of course be repeated several times, especially when samples of air from very different sources are successively analysed.

"Concerning the technical making of the apparatus the following may be said: —

"The three reservoirs *A*, *B*, and *C* form, with the connecting glass tubes, a single system. I order them from Franz Müller, in Bonn, Germany, who furnishes them at low prices and carefully made. I have preferred to have *A*, *B*, and *C* sent to me in separate pieces. I myself then fill *B* with phosphorus pentoxide and *C* with soda-lime, and also calibrate the graduated tube of the pipette *A*. The three reservoirs are then fastened with string in the proper position on a thin board. At the two places where the tubes are to be fused together large holes are cut in the board, so that the ends of the glass tubes, which must be pushed close together, may be reached with the flame from all sides. After first warming them with an alcohol lamp, the glass tubes may be easily and tightly fused together with the help of a blast-lamp or a small gas blow-pipe. In this way it is easily possible without further practice to put together much more complicated pieces of glass apparatus. One might perhaps just as well order from the manufactory reservoirs which are already filled and joined together. The ordinary Geissler stopcocks are usually made with sufficient care to enable them to withstand the pressure arising in the apparatus.[1] But since the slightest error makes the whole apparatus useless, Müller has made stopcocks of longer and less conical surface; these answer the purpose admirably. The tube connecting the glass stopcock λ with the movable mercury reservoir has to withstand a high internal pressure. For this purpose I use an ordinary rubber tube not too thin-walled — either red or black rubber is the best — and surround it with a spiral of flexible copper wire, as shown in Fig. 105. Such tubes are very easy to make, and they last for several years even when they have to withstand an internal pressure of more than one atmosphere. The glass connecting tubes and stopcocks should have openings not less than 1 mm. in diameter.

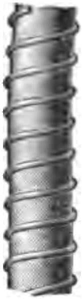

FIG. 105.

"The moisture in the atmosphere is usually determined with psychrometers and from the readings of the dry and wet thermometer, — the psychrometrical difference, — and with the help of empirically derived formulas and tables the result is expressed as the moisture pressure in millimeters of mercury. Since determinations of moisture can be easily and accurately carried out with my apparatus, I have made a number of parallel researches with psychrometer thermometers from the Central Meteorological Station. The agreement is generally good when the temperature of the air is not too low. In this case the psychrometric method, as is well known, cannot be used, because the differences become too minute or at times negative. On this account when scientific expeditions have spent the winter in arctic regions they have usually been obliged to give up the determination of the atmospheric moisture. I hope that in such cases, and generally in meteorological determinations of the moisture in the air, the apparatus described above, but of very much smaller dimensions, may do good service. The most natural and simple method for determining the moisture of the atmosphere is to directly ascertain the volume per cent of the aqueous gas or vapour without necessity of corrections for pressure or temperature. It is these corrections probably which deter chemists from using the other absorption methods for the determination of atmospheric moisture (Schwackhöfer's apparatus, etc.).

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[1] *N.B.* — If they are not too conical in form.

"The determination of the carbon dioxide in air is in itself so difficult that one must be prepared to use either relatively large apparatus or an inconvenient equipment and method of work. Instead of giving a résumé of the many methods and proposals in this line, I will call attention only to the experience of Professor W. Spring in his well-known and admirable work upon the determination of the carbon dioxide in the air at Lüttich. Professor Spring carefully tested all of the methods in use, and the only method which he found good was the chemical determination of carbon dioxide with barium hydroxide; the various volumetric methods could not be recommended because of the unfitness of *liquid* absorbents.

"For this reason I have used as absorbents *dry* phosphorus pentoxide and *dry* soda-lime, of which the former absorbs only water, the latter only carbon dioxide and water. As, however, I fully agree with Professor Spring that the chemical method (titration) is the most reliable of all the older methods, I have taken the trouble to obtain a series of parallel analyses by my method and by Pettenkofer's method in its latest improved form. Herr C. Sondén, Engineer and Chemist of the Hygienic Bureau in Stockholm, has been so kind as to make simultaneously with me, upon certain days in November and December, 1885, determinations of the carbon dioxide in the air, using for the purpose large quantities (10 liters) of atmospheric air. The samples of air were taken on the balcony of the laboratory of the High School, which is quite centrally located in Stockholm.

"At the same time psychrometric determinations of the atmospheric moisture were made with the instruments from the Central Meteorological Station.

Date			Determinations of Water		Determinations of Carbon Dioxide	
Month	Day	Time	Psychrometer	Pettersson's Methods		Pettenkofer's Method (Sondén).
			Per cent	Per cent	Per cent	Per cent
November	1	11.22	...	0.968	0.059	...
"	8	10.50	0.86	0.801	0.055	0.052
"	15	2.25	0.41	0.461	0.039	...
"	22	10.55	...	...	0.043	...
"	27	11.44	0.46	0.479	0.044	...
December	5	10.17	0.67	0.718	0.041	0.044
"	6	10.16	0.24	0.219	0.046	0.043
"	8	9.26	0.22	0.213	0.051	0.056
"	"	"	...	...	...	0.059
"	"	"	...	...	...	0.066
"	9	9.90	0.25	0.150	...	...

“As already stated, the figures given by the psychrometer generally agree quite well with the analytical results; a noticeable difference was seen only on the 9th of December, when the temperature of the air was rather low (below -8° C.). A greater agreement between the determinations of carbon dioxide by such different methods could hardly be expected.

“From among the many analyses of the air of the laboratory, which in themselves are of but little interest, I will give some results obtained during the preceding week:—

May 6.	Moisture	=0.640	per cent	Carbon dioxide	=	...
“ 7.	“	=0.687	“	“	=0.134	per cent.
“ 8.	“	=0.877	“	“	=0.113	“
“ 9.	“	=0.815	“	“	=0.109	“
“ 10.	“	=0.754	“	“	=	...

“I am endeavouring at the present time to apply the same analytical principle to the determination of oxygen in the atmosphere, and I hope later to be able to publish something on that subject.”

For the determination of carbon dioxide, Otto Pettersson and A. Palmqvist have materially simplified the apparatus just described. They describe the new apparatus as follows:—

“Under the heading, ‘The analysis of air upon a new principle,’ published in the *Zeitschrift für analytische Chemie*, **25**, pp. 467 to 478, one of us has described an apparatus for volumetrically determining the amounts of moisture and carbon dioxide in the air directly, without corrections for variations of temperature and pressure. Since we desired to make use of this principle for the sanitary determination of carbon dioxide, which is made almost exclusively by the exact but rather complex and long method of Pettenkofer, we have endeavoured, with the coöperation of C. Sondén, to give to the apparatus described by Pettersson a simpler and more convenient form, and if possible to reduce the length of each determination from a half hour or more, down to a few minutes. This was accomplished by analysing the air not in an absolutely dry condition, but saturated with moisture. The complete drying of the air can be done only with phosphorus pentoxide, and this takes considerable time. When dry absorbents are used the absorption must take place under considerably increased pressure, a circumstance which calls for great care in the making of the apparatus, the construction of the glass stopcocks, the introduction of the absorbents, etc. In using moist air we must give up, it is true, the direct determination of the water vapour, but, on the other hand, it becomes possible to make a direct determination of the carbon dioxide by means of a liquid reagent, and the analysis is completed in a few minutes without the tubes being exposed to any appreciable increase of pressure.

"Figure 106 shows the apparatus which we used, and which is easily portable. The apparatus can be covered by a wooden box which fits over it, and to which a metal handle is strongly fastened (this cover is not shown in the figure). When the apparatus has been brought to the place where the air is to be examined, the glass jacket is filled with water, the outside air is drawn in through the tube *c*, and by

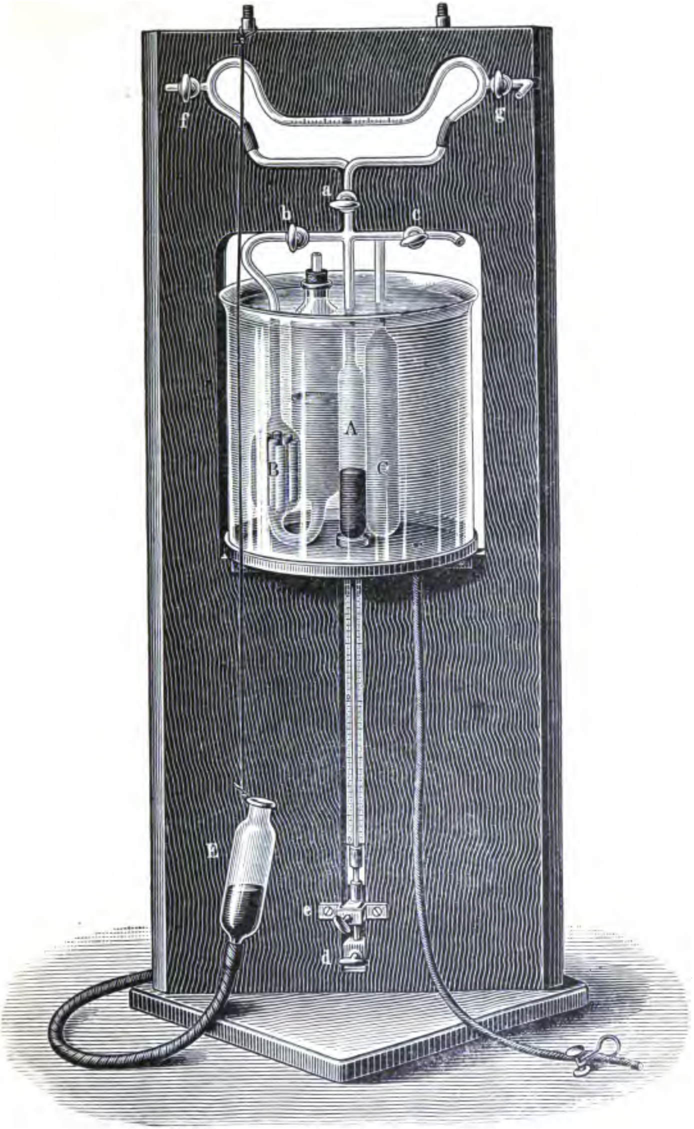
f
g
a
b
c
A
B
C
E
e
d

FIG. 106.

a few simple manipulations, which take only a few minutes, the carbon dioxide is determined with an accuracy of about 0.01 per cent. The dimensions of the apparatus are as small as possible. For example, the pipette *A* into which the air to be analysed is drawn holds only about 18 ccm. With larger volumes of air it would be easy to attain greater accuracy.

"The carbon dioxide is absorbed in the Orsat potash-tube *B*, and the air is measured, before and after the absorption, in the pipette *A* and its graduated tube. The measuring pipette can be filled with mercury or air, or emptied of the same, by raising or lowering the mercury reservoir *E*, which is joined to the lower end of the graduated tube of *A* by means of a rubber tube wrapped with copper wire. There must always be a drop of water on the surface of the mercury; the air standing over the mercury is thus kept saturated with moisture. In reading the volumes, the meniscus of the mercury is each time so adjusted that the pressure in *A* is exactly the same as the pressure of the air in the compensation cylinder *C*.

"A differential manometer containing a drop of a coloured liquid (petroleum, in which azo-benzol is dissolved), and connected by capillary glass tubes on the one side with *A* and on the other with *C*, serves as the indicator in these operations. By moving the reservoir *E* and then — having closed the stopcock *d* — suitably turning the screw *e*, the level of the mercury in *A* is so adjusted that the drop of liquid in the manometer stands at zero. It is obvious that in this manner it is always possible to bring back the air in *A* to the same pressure as that prevailing in the compensator *C*. Since the air in both the compensator and pipette is, from the beginning of the experiment, separated from the external atmosphere by closing the stopcocks *f*, *g*, and *c*, any variations in the external atmosphere have no effect. This is also true of changes in temperature; these eliminate themselves by acting in the same manner and to the same extent upon the tension of the air in *A* and *C*, provided that the water in the outer vessel which surrounds the main parts of the apparatus is sufficiently stirred. For these reasons no observation of temperature or barometric pressure is necessary. The changes in volume read off on the scale give directly the amount of carbon dioxide in hundredths of per cent by volume.

"Since the air is saturated with moisture before the absorption, it is clear that for strict correctness a slight correction is necessary to reduce the per cent of carbon dioxide found in the air saturated with moisture to the proper figure for the air in its actual condition. This simple correction is, however, of no importance because it is so small. An example will make this clear. Let us suppose that the temperature is 23° C., and that the air is so dry that it contains only 0.66 per cent of water vapour at a barometric pressure of 760 mm. The actual amount of carbon dioxide present is then ascertained by means of the equation: —

$$x : (100 - 0.66) = 0.04 : 100$$
$$x = 0.039736.$$

The result of the analysis is, therefore, 0.000264 too high.

"Each analysis consists of three operations.

"1. The air is drawn in from the outside and is measured, the level of the mercury in the graduated tube being brought to the zero mark. The upper and narrower part of the scale, where each division denotes $\frac{1}{10000}$ of the volume of the pipette, is used in analyses of atmospheric air, or the ordinary air of rooms, where the per cent of carbon dioxide is at the most not higher than 0.4 per cent. In the analysis of very impure air the lower part of the graduated tube is used, each division here corresponding to $\frac{1}{1000}$ of the whole volume. In measuring the volume the stopcocks *f*, *g*, *b*, *c*, and *d* must be closed.

"2. The stopcocks *d* and *b* are opened, *a* is closed, and the air is passed from *A* to *B*. After one or two minutes the carbon dioxide is absorbed and the air may be brought back into *A*, *b* is then closed, and *a* is opened.

"3. The mercury level in *A* is so adjusted that the index again takes its normal position. The decrease in volume is then read off on the scale.

"The following table contains some parallel determinations which were simultaneously made with the same samples of air: (1) with the apparatus just described; (2) with a larger apparatus constructed upon the same principle by Sondén; and (3) by Pettenkofer's method. It is worthy of mention that in such parallel analyses, if they are to give results really exact to 0.01 per cent, the air must not be taken directly from the room, because the air of a room is not always homogeneous. The air samples must be taken from volumes of air confined in special reservoirs.

Series of Experiments		Determination of Carbon Dioxide with the Portable Apparatus	Determination of Carbon Dioxide with Sondén's Apparatus	Determination of Carbon Dioxide by Pettenkofer's Method
I.	a	0.030 per cent	0.041 per cent	...
	b	0.030 "	0.038 "	...
II.	a	0.460 "	0.463 "	...
	b	0.450 "	...	...
III.	a	0.195 "	0.211 "	0.22 per cent
	b	0.205 "	0.206 "	0.21 "
	c	0.210 "	0.210 "	...
IV.	a	0.230 "	0.227 "	0.23 "
	b	0.225 "	0.223 "	0.23 "
	c	0.220 "	...	...
V.	a	0.080 "	0.077 "	0.10 "
	b	0.070 "	...	0.09 "
VI.	a	0.170 "	0.170 "	...

"Any impurities in the measuring tube may be easily removed by rinsing the pipette with water which is drawn in and driven out through *c*.

"We would in passing call attention to the fact that the Pettenkofer method can be very much shortened by closing the bottle in which the water is to be shaken with the barium hydroxide solution, not with a cap but with a tightly fitting perforated rubber stopper, through which is inserted a glass tube reaching to the bottom of the bottle. This glass tube has, at two or three different places, loosely inserted stoppers of pure cotton.

"After shaking the bottle, the glass tube can be connected with the branch tube of a glass stopcock burette, and the excess of barium hydroxide can be drawn up into the burette and immediately titrated.

"The baryta water may be somewhat cloudy after passing the first stopper of cotton, but it is filtered by the second and third, and enters the burette perfectly clear.

"Sulphur dioxide can also be titrated in the same way."

3. *Carbon Monoxide*

On account of the very poisonous nature of carbon monoxide it is important in sanitary examinations of the air to determine the absence or presence of this gas. The blood reaction, which is fully described on p. 211, is best adapted to this purpose.

4. *The Determination of Oxygen in the Atmosphere*

The great significance which the oxygen in the atmosphere has for all living beings has made the determination of this gas the subject of frequent investigations.

Of the many methods which have been used for this purpose, that one which was original with Jolly and was elaborated by Kreusler is one of the most exact. In 1886 and 1887 the author, in coöperation with Kreusler and Morley, made a number of analyses of atmospheric air.. In these investigations Kreusler determined the oxygen by causing it to unite with glowing copper, Morley by combustion with hydrogen, and the author by absorbing the oxygen with alkaline pyrogallol. By paying great care to all the necessary precautions, closely agreeing results were obtained by the three different methods.

The description of the method used by the author is given below.

THE DETERMINATION OF OXYGEN WITH THE HEMPEL APPARATUS FOR EXACT GAS ANALYSIS[1] (p. 79)

The arrangement of the apparatus has already been described in detail, so that only a few particulars that are of importance in very accurate work will here be given.

The samples of air were collected in glass tubes which had been previously exhausted of air, as described on p. 6. The glass tubes were opened in a small mercury trough by breaking off the end of the tube with ordinary pliers. A small crucible was then slipped under the tube, and the tube was thus lifted out and put in a cylinder. The air was then drawn over into a gas pipette containing a very little water. This pipette was kept where it was somewhat warmer than the room in which the analysis was to be made. On days when the gas laboratory had to be heated, the pipette stood near the heating tube. In this simple manner the gas to be analysed was saturated with water, so that later it was not necessary to moisten the measuring bulb. The measuring bulb was cleaned before each determination, and after being dried it was brought into the mercury-trough of the apparatus by placing it in two porcelain crucibles, one within the other (see Fig. 107), and filling these with mercury. If these are then lowered through the cooling water of the trough into the mercury, and the longer crucible removed by lowering it still further, the measuring bulb may now be lifted out of the small crucible under the surface of the mercury without a trace of water entering it. If only one crucible is used, water may easily get into the bulb, the probable cause being surface adhesion. With the instrument shown in Fig. 108 the air was then sucked out of the measuring bulb and the gas sample was passed in from the gas pipette, great care being taken that no trace of water entered the bulb.

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1885, 267; 1887, 1834.

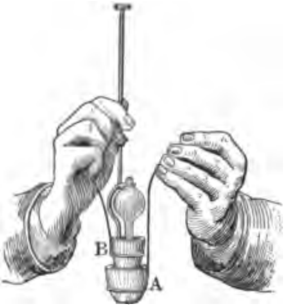

FIG. 107.

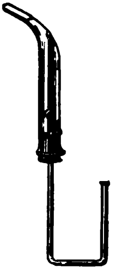

FIG. 108.

The readings of the pressure on the scale of the barometer tube were repeated every three minutes until there was no difference between two readings.

The pipette was filled with alkaline pyrogallol with the apparatus described on p. 153. After filling, the capillary of the pipette was placed in a beaker of water, and the capillary was freed from the reagent by carefully drawing in and driving out a little water.

When this washing was completed, as may be told with ease from the formation of the streaks in the water, the capillary of the pipette was placed in a beaker of fresh distilled water and a water-thread about 3 mm. long was drawn in. The capillary was then carefully dried on the outside. The gas was next drawn over into the pipette thus made ready, and the absorption of the oxygen was effected by shaking the pipette for five minutes. The advantage of the short thread of water in the capillary is that when the gas is drawn into the pipette the water once more rinses the capillary throughout its entire length.

After the absorption another short thread of water was drawn into the capillary by immersing the latter in distilled water, the pipette was then brought into position in the apparatus, and before driving the gas back into the measuring bulb mercury was sucked into the pipette through the capillary, the mercury driving the little thread of water before it. Upon blowing into the pipette the gas now passes into the measuring bulb, being saturated with water vapour in its passage through the freshly moistened capillary.

It is thus easy to prevent any trace of the reagent from entering the measuring bulb. The agreement of the results is quite remarkable. The pipette must be frequently cleaned by drawing water into it so that muddy particles will not adhere to the glass.

An idea of the accuracy which can be attained by this method may be formed from the following figures.

In analyses of air samples kept in fused glass tubes my assistants, working more than a year apart, found —

	Oettel	Schumann (One year later)
Air of April 14, 1886 . . .	20.89 per cent	20.89 per cent
Air of April 5, 1886 . . .	20.93 "	20.94 "

In four analyses of the same sample Oettel found —

20.936 per cent	20.938 per cent
20.938 "	20.938 "

To permit of a comparison between the combustion method with copper and the absorption method with alkaline pyrogallol, Herr Kreusler had the kindness to collect samples on three different days and to send them to Dresden. These samples were first analysed by my method by Herr Oettel in Dresden, and later by Herr Tacke and Herr Kreusler in Bonn. The results are given on p. 150.

5. *Ozone*

For the detection and determination of ozone, see p. 161.

6. *Argon*

For details concerning Argon, see p. 168.

7. *Sulphur Dioxide and Sulphuric Acid*

To detect very small amounts of sulphur dioxide and sulphuric acid in the atmosphere Ost recommends that pieces of linen cloth be dipped into strong baryta water, then treated with carbon dioxide, and that these strips be hung up in the air for several weeks or months. The presence of sulphuric acid in the cloth is then detected by burning the cloth and testing the ash. H. Wislicenus found that it was necessary to first treat the cloth with hydrochloric acid and water to free it from all sulphur compounds which it might contain. The detection and determination of the sulphuric acid is carried on by first incinerating the cloth and then fusing a part of the ash with sodium carbonate to transform the barium sulphate into sodium sulphate and barium carbonate. The sodium sulphate is then extracted with water, and the sulphuric acid is determined in the usual manner by precipitation as barium sulphate.

8. *Nitrogen*

Up to the present time no convenient and accurate method for determining free nitrogen is known.

CHAPTER VIII

EXAMINATION OF THE GASES WHICH ARE PRODUCED BY LIVING BACTERIA

W. HESSE has carried on in the author's laboratory a long series of investigations upon the gases evolved from growing bacteria.

From the very nature of the case it is apparent that in such an examination we must endeavour to work with as small quantities of substance as is possible.

Hesse used the apparatus shown in Fig. 109 for the bacteria cultures. This consists of a small Erlenmeyer flask of about 50 ccm. contents, in the neck of which is inserted a glass stopper carrying two glass tubes after the manner of a Drechsel wash-bottle. Each tube is provided with a carefully ground glass stopcock, a tube beyond each stopcock being capillary. If it is desired to avoid any possibility of the passage of gas through the lubricant of the stopcocks, these may be given the form shown in Fig. 74 *c* and *d* on p. 171, which permits of their being covered by

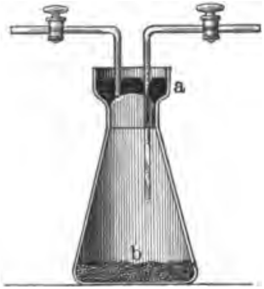

FIG. 109.

mercury. The stopper of the flask is also covered with mercury in the manner shown in Fig. 109.

A suitable culture medium *b* is placed in the flask and this is then inoculated with the bacteria which are to be examined. The apparatus renders it possible to carry on the culture in air or in any other desired gas, the gas being led into the flask through the stopcocks. To examine the gas which may be set free during the growth of the bacteria, the apparatus is connected by means of a three-way capillary (Fig. 40) with a gas burette of the construction shown in Fig. 36, III. The widening of the lower portion of the measuring tube of the burette renders it possible to employ the burette as an aspirator and to easily draw out from the flask 10 ccm. of the gas which it contains.

This gas is measured in the burette and is then brought into contact with the proper absorbents in small pipettes, every trace of air being excluded throughout the analysis by the use of the three-way capillary shown in Fig. 40. All operations are performed over mercury, and the pipettes are filled with mercury and the reagents. The bulbs of the pipettes need not have a greater capacity than 20 cc., and they may have the form shown in Figs. 31 and 32 or Figs. 37 and 38.

CHAPTER IX

THE DETERMINATION OF FLUORINE AS SILICON TETRAFLUORIDE

At the suggestion of the author, O. W. F. Oettel has worked out a method for the determination of the fluorine in a substance, the fluorine being evolved as silicon tetrafluoride, and the volume of this gas then being directly measured. Since a large number of substances contain both fluorine and carbon dioxide, the author and W. Scheffler[1] have devised a method which permits of the simultaneous determination of fluorine and carbon dioxide in a single sample. The fluorine is set free as silicon tetrafluoride together with carbon dioxide in a suitable apparatus, is collected in a burette, and the silicon tetrafluoride is then decomposed and absorbed by means of water (a small volume of carbon dioxide is here taken up by the water). The carbon dioxide still present in the gas is then completely removed by passing the gas into a pipette containing caustic potash. The gas residue is again brought over the water which was first used and by which the silicon tetrafluoride was absorbed; the absorbed carbon dioxide hereupon escapes from the water and passes into the gas residue. Upon transferring the gas once more to the caustic potash pipette, the remainder of the carbon dioxide is removed, and this volume is subtracted from the diminution first obtained by the absorption with water. The difference gives the amount of silicon tetrafluoride.

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[1] Walther Hempel and W. Scheffler, *Zeitschr. f. Anorgan. Chemie*, 1897, **20**, 1.

In this manner it is possible to make very sharp determinations of fluorine in the presence of carbon dioxide.

For setting free the silicon tetrafluoride there is used the apparatus shown in Fig. 110, II, which has already been described on p. 75, Fig. 42. The evolution flask is connected with a simple gas burette filled with mercury and containing on top of the mercury some concentrated sulphuric acid. It is well to join to the burette a level-bulb instead of a level-tube, and to attach a glass stopcock to the lower end of the burette tube (see Fig. 110).

The substance under examination is mixed with finely powdered quartz, the weight of the quartz being fifteen times that of the fluorine which is probably present in the material. The quartz is first heated for a long time in a muffel furnace under free access of air to remove every trace of organic matter.

The sulphuric acid to be employed must be freed from organic substances and from oxides of nitrogen. This is accomplished by adding to the concentrated sulphuric acid about 5 g. of powdered sulphur and then fuming down the acid to two-thirds of its original volume.

In carrying out a determination the evolution flask II is first carefully dried and the substance, together with the proper amount of quartz powder, is then introduced into the flask by means of a long weighing tube, and the two powders are mixed as intimately as possible by shaking the flask. The flask is then joined by means of the capillary *d* and a

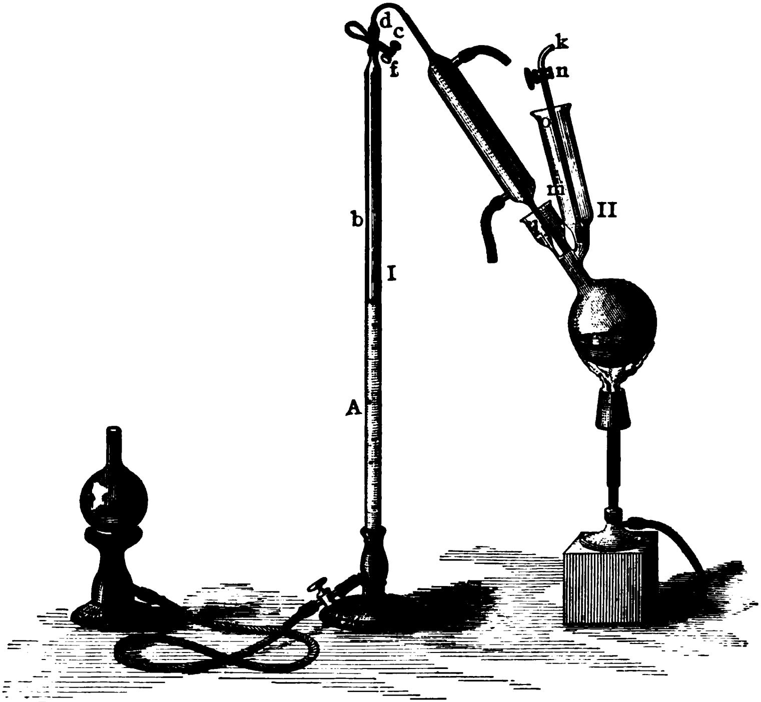

FIG. 110.

piece of dry rubber tubing to the gas burette I which contains mercury and some sulphuric acid, as above described. The rubber tube is held firmly in place by means of ligatures of light iron wire. The volume of concentrated sulphuric acid which is placed in the pipette amounts to only about 0.25 ccm. Its presence is necessary to avoid the possibility of decomposition of the silicon tetrafluoride by any moisture that might be in the burette.

In the bells *l* and *m* is placed some of the highly concentrated sulphuric acid. A water suction pump is now connected to *k*, and the flask II is partially exhausted. The stopcock *n* is then closed, and upon lifting the tube *o* sulphuric acid flows down from *m* into the flask. The flask is shaken so as to bring the acid into intimate contact with the mixture of quartz and the substance, and the contents of the flask is then heated fully up to the boiling-point of sulphuric acid, the heating being continued for about fifteen minutes.

If the apparatus should break, the operator might be seriously injured by the hot concentrated sulphuric acid. It is well, therefore, to protect the eyes with goggles, and to place a glass screen between the flask and the operator.

The heating is now stopped, and the gas in the flask is completely driven over into the burette by filling *m* with some of the concentrated sulphuric acid and carefully lifting the tube *o*. The flask is then disconnected from the burette and the total volume of the evolved gases is measured.

The burette is now connected in the ordinary manner, by means of a capillary tube, with a simple mercury absorption pipette of the form shown in Fig. 111, the pipette containing 5 ccm. of water above the mercury. The gas is transferred to the pipette and shaken for five minutes with the water.

It is then brought back into the burette and the diminution in volume is read off.

The remaining gas is passed into a pipette filled with a solution of potassium hydroxide to absorb carbon dioxide, and is then drawn back into the gas burette. The volume is observed, and the gas is now passed into the first pipette, Fig. 111, and shaken again for three minutes. It is then passed back into the burette, and the residual volume of gas is measured. This gas is then passed once more into the potassium hydroxide pipette to determine the small amount of carbon dioxide which was taken up by the water used in the first absorption of the silicon tetrafluoride.

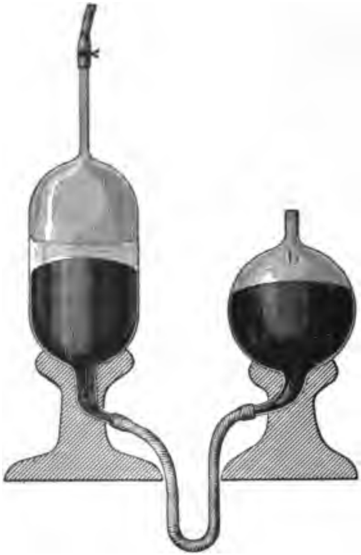

Fig. 111.

All of these operations can be carried out with considerable speed, and it is therefore easily possible to make a determination of fluorine in two hours.

As an example of the accuracy of the method, the following result may be cited: 2.156 g. of the substance gave 3.56 ccm. of silicon tetrafluoride, while theory called for 3.45 ccm.

ANALYSIS OF TEETH

It was found upon experiment that both calcium fluoride and sodium fluoride lost weight when heated to about 1000°.

1.495 g. of calcium fluoride lost upon ignition at 1000° for fifteen minutes 0.019 g., at red heat 0.0005.

4.367 g. of sodium fluoride lost at 1000° 0.104 g., at red heat 0.00075 g.

Experiments were then made to ascertain whether it is possible to incinerate teeth without loss of fluorine. With this object in view, finely pulverised teeth were burned in a combustion furnace in a current of oxygen. A roll of fine-mesh platinum wire-gauze 5 cm. long was placed before the layer of the substance, and behind the substance there was a 10 cm. layer of pieces of marble as large as peas. During the combustion, these pieces of marble were heated to about 100°. The purpose of their introduction is to retain any calcium fluoride or sodium fluoride which might be volatilised. After that part of the tube in which the platinum wire-gauze is placed has been heated to bright redness, the substance is heated little by little in a slow current of oxygen, and all organic substance is completely burned. The marble showed no trace of fluorine when examined after the conclusion of the experiment.

The incineration of teeth is easily effected in a hard glass tube in a current of oxygen if the powder is very fine and is placed in the tube in a very thin layer.

In determining fluorine in material which contains organic matter, it is very important that the substance should be completely incinerated, since the slightest trace of residual carbon would act upon the boiling sulphuric acid and cause the formation of sulphur dioxide, a gas which would then be absorbed by water when the silicon tetrafluoride is determined. In the analysis described below, the teeth were incinerated in the manner just mentioned.

HORSES' TEETH

Analysis I

2.332 g. of the ash of the teeth was decomposed in the apparatus shown in Fig. 110. The evolved gas, on shaking with water, gave a diminution of 2.05 ccm.; in a caustic potash pipette, 16.12 ccm. of carbon dioxide; on shaking the gas residue with the water which had been used for absorbing the SiF_4, an increase in volume of 0.95 ccm., of which 0.65 ccm. was absorbed by caustic potash. The volume of SiF_4 is, therefore, $2.05 - 0.65 = 1.4$ ccm., corresponding to 0.2 per cent fluorine.

Analysis II

2.274 g. of the teeth ash gave with water a diminution of 3.2 ccm.; and, after subtracting the carbon dioxide absorbed by the water, 2.6 ccm. SiF_4, corresponding to 0.39 per cent fluorine. The carbon dioxide originally contained in the gas mixture amounted to 15 ccm.

Analysis III

2.419 g. of the teeth ash gave, after subtracting the carbon dioxide, 2.2 ccm. SiF_4, corresponding to 0.31 per cent fluorine. The carbon dioxide contained in the original gas mixture amounted to 15.9 ccm.

HUMAN TEETH

Two samples of unsound teeth and four samples of sound teeth were examined. Two teeth were used in each analysis, and were incinerated separately. The results follow: —

Human Teeth	Grams of Teeth Ash taken	SiF_4 + CO_2 found	CO_2	CO_2 which was taken up by the water	SiF_4 in cubic centimeters	Fluorine in Grams	Per cent of Fluorine in the Teeth Ash
Unsound	1.793	1.0	4.65	. . .	1.0	0.0034	0.19
Sound	1.434	1.5	5.80	0.4	1.4	0.0047	0.33
Sound	0.831	1.6	3.50	. . .	1.6	0.0054	0.52

CHAPTER X

APPARATUS FOR THE ANALYSIS OF SALTPETER AND THE NITRIC ACID ESTERS (NITRO-GLYCERIN, GUN-COTTON, ETC.)

WALTER CRUM[1] has found that the nitrogen acids dissolved in sulphuric acid (nitrogen trioxide, nitrogen peroxide, and nitric acid) are completely reduced to nitric oxide by shaking with mercury at ordinary temperatures. John Watts[2] and Georg Lunge[3] have worked out this method still further, and the latter has constructed an apparatus therefor which he calls a nitrometer. The author first[4] used the reaction for the decomposition of the nitric acid esters, and in particular for the determination of the nitro-glycerin in dynamite. Lunge has determined the conditions under which it is possible to analyse saltpeter in the same manner.

The above-mentioned analyses may be easily carried out in the apparatus here described (Fig. 112).

The apparatus consists of the evolution cylinder *c*, the level-bulb *e*, and the gas burette *ab*. *c* has at the top a glass stopcock *i*, and near the bottom a side tube *x*. It is closed by a double-bore rubber stopper, over which passes a metallic band to keep it from being

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[1] *Ann. d. Chem. u. Pharm.*, **62**, 233; also *Jour. f. prakt. Chemie* **41**, 201.

[2] *Chemical News*, **37**, 45.

[3] *Berichte der deutschen chemischen Gesellschaft*, **11**, 434.

[4] *Zeitschrift für analyt. Chemie*, **20**, 82.

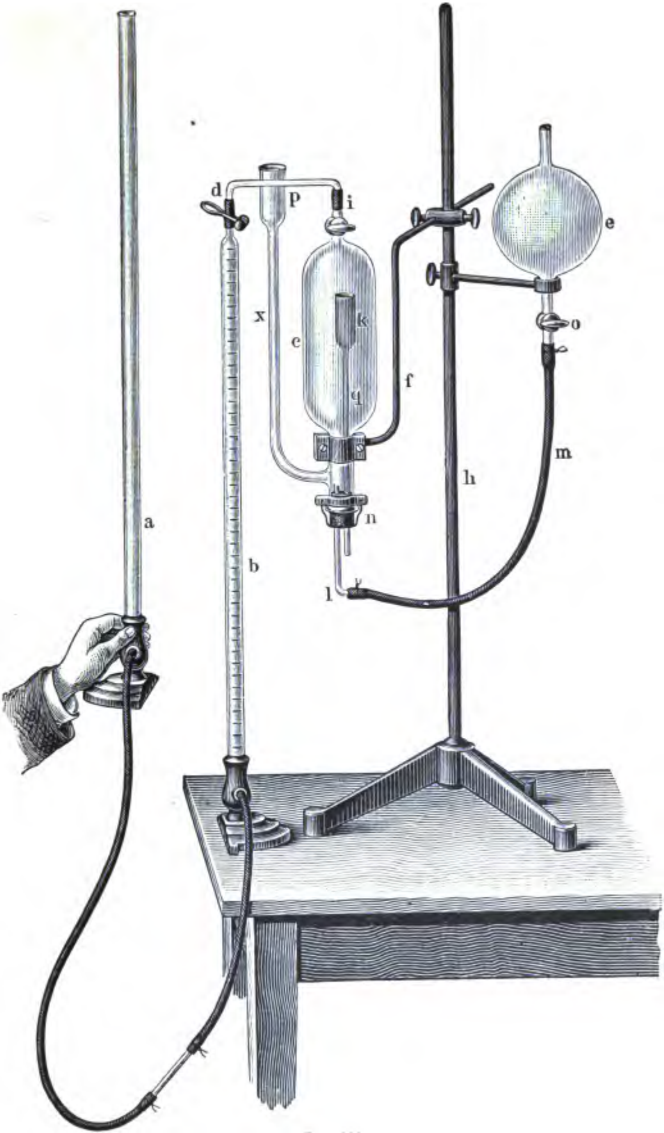
d
p
i
e
x
k
c
o
q
f
m
h
a
n
b
l

FIG. 112.

forced out by the pressure of the mercury. The long handle of the weighing-tube *k* passes through one opening of the stopper, and through the other is inserted the bent tube *l*, which is joined to the level-bulb *e* by the rubber tube *m*. The bulb *e* is supplied with a glass stopcock *o*.

To use this apparatus for the evaluation of dynamite or other nitric acid ester, fill the bulb *e* completely with mercury, *o* being closed; insert *k*, containing the weighed substance, in the rubber stopper, and put the apparatus together as shown in Fig. 112. The gas burette, however, is not yet connected with *i*. By opening *o* and *i* and raising *e*, *c* is completely filled with mercury. The stopcock *i* is then closed. If now the sulphuric acid required for the decomposition be poured into *x*, the acid may easily be brought into *c* by lowering the bulb *e*. The entrance of the sulphuric acid can be stopped at any moment by closing the stopcock *o*, and the introduction of air may be very easily avoided.

Atmospheric pressure is then reëstablished in the apparatus by raising *e* and opening *o*, and *c* is shaken until, with stopcock *o* closed, no rise of mercury can be observed in *x* after renewed shaking.

When, with *o* closed, the mercury in *x* remains at the same height after two shakings of *c*, the reaction is ended. The cup *k* should be just deep enough to easily hold the substance; it is desirable to have cups of different sizes to correspond to the volume of the material to be analysed.

When the evolution of gas is complete, *c* is connected with the gas burette, which is filled with mercury, and which has been previously moistened with a very little water. The nitric oxide is then drawn into the burette by opening *o*, *i*, and *d*, and raising the bulb *e*. The gas is then measured in the usual manner, with allowance for the tension of the water vapour, and the calculation is made.

To clean the apparatus, drive as much of the mercury as possible back into the bulb *e*, close *o*, and open the cylinder *c* over a large beaker of water so as to catch the mercury, and at the same time separate it from the sulphuric acid. *c* is rinsed out with water, and after drying the weighing tube *k*, the apparatus is ready for a new determination. If the warming of the gas burette with the hands has been avoided, the measurement can be made in a very few minutes. The readings are, of course, very sharp, because there is no sulphuric acid in the gas burette.

To test the purity of the nitric oxide obtained, the gas is led into a double gas pipette containing a solution of a ferrous salt; the evolved carbon dioxide may be absorbed in a pipette containing potassium hydroxide solution.

The analytical absorbing power of a saturated solution of ferrous chloride is 14, of ferrous sulphate 3 to $4\frac{1}{4}$.

To analyse saltpeter in the above apparatus, the substance must first be dissolved in a very little water.

E. B. Hagen has used the apparatus very often for the analysis of gun-cotton, and has devised for this purpose a manipulation which admits of very accurate and easy work.

Hagen purposely moistens the vessel *c*, if it is not already sufficiently moist from the preceding analysis, and then introduces into the inverted apparatus a weighed amount of gun-cotton, which has previously been finely divided with a knife or rasp. The apparatus is then put together, the gun-cotton adhering to the walls of the vessel because of the moisture present. *c* is then placed in a slanting position, as shown in Fig. 113, and mercury is run in until only a few cubic centimeters of air remain in the cylinder. The stopcock *o* is now closed and *c* is shaken. This thoroughly moistens the powder with water. The air is now completely driven out of *c* by allowing the mercury to enter.

After the introduction of the concentrated sulphuric acid *c* is shaken for three minutes, and when the gun-cotton is dissolved in the acid *c* is heated directly with the Bunsen burner (Fig. 113), and is shaken as long as evolution of gas results. The nitric oxide which is set free is now measured in the manner previously described. Many samples of gun-cotton contain some calcium carbonate, and hence the possibility of the presence of some carbon dioxide should be not overlooked.

Especial attention should be called to the fact that too much sulphuric acid must not be used: 15 ccm. suffices in all cases. On account of the solubility of nitric oxide in sulphuric acid, a correction depending upon the amount of acid used must be brought into the calculation. For 15 ccm. of sulphuric acid 0.21 ccm. is to be considered as having gone into solution. The advantage of the apparatus lies in the great speed with which the work may be done. If the burette stand where the temperature is uniform, and if the apparatus be brought near the burette only for the purpose of transferring the gas, then two analyses may easily be made in an hour, since under these circumstances the readings of the gas volumes may be made after ten minutes at the longest.

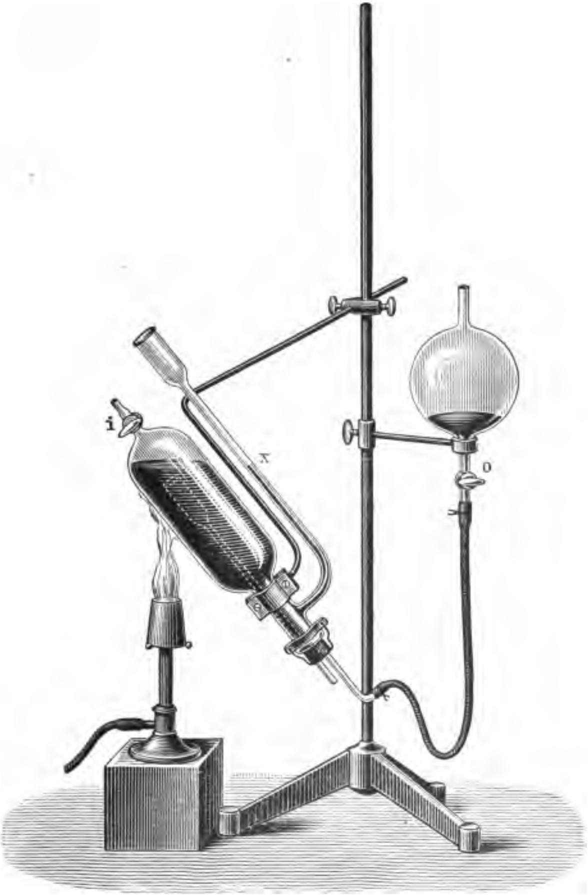

Fig. 113.

CHAPTER XI

THE DETERMINATION OF CARBON AND HYDROGEN, AND THE SIMULTANEOUS VOLUMETRIC DETERMINATION OF NITROGEN, IN THE ELEMENTARY ANALYSIS OF ORGANIC SUBSTANCES

IF the combustion of substances containing nitrogen be carried out, not in tubes filled with carbon dioxide or hydrogen, as in the methods of Dumas and Bunsen, but in complete vacuum, it is then possible — provided that after the combustion the tube is again exhausted and the combustion products collected — to weigh the carbon dioxide and water and to measure the nitrogen.

In addition to a combustion furnace, a tube filled with copper oxide, metallic copper, and the substance to be analysed, and absorption apparatus for carbon dioxide and water, the method to be described calls for an air-pump and a graduated tube for measuring the nitrogen.

The mercury air-pump constructed by Professor Töpler[1] possesses neither stopcocks nor valves nor dead space, and is therefore especially suited for this work.

This air-pump is a combination of three barometers, two of which act as valves, while the third, analogous to the Geissler pump, ends in a thick-walled bulb by means of which the vacuum is produced. The arrangement is shown in Fig. 114.

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[1] Dingler's *Polyt. Jour.*, **163**, 426 (1862).

In the drawing, *ga* is a wide glass tube ending in the glass bulb *A*, and joined by a wide rubber tube *nf* with the large bulb *D*. From the upper end of *A* a narrow bent tube *qbc* passes downward into *G*. The length of this last-named tube, from the highest point *b* to the open end *c*, is somewhat more than the greatest barometric height of the locality.

From just below the bulb *A* rises the small tube *as*, whose highest point is considerably more than the barometric height above the highest point of the tube *qbc*. At *s* this tube bends downward again and is permanently connected with the receiver *B*. The whole system of tubes from *g* to *s* can easily be put together by a glassworker; it is fastened to a suitable wooden standard, which is provided at different levels with supports for the mercury reservoir *D*, so that *D* can easily be brought into any desired position.

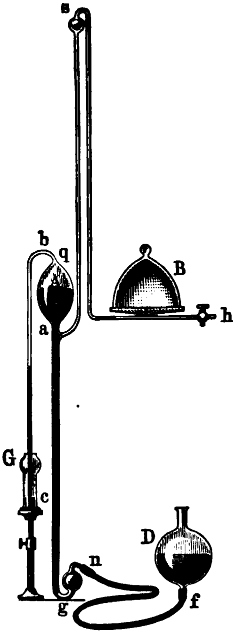

FIG. 114.

D is filled with mercury, and so much mercury is poured into *G* that the end of *bc* is about 1 cm. below the surface. The apparatus is then ready for use.

Regarding the use of the apparatus, a discrimination must be made between two distinct manipulations: —

1. If *D* be raised to the height of the bulb *A*, the air in the latter will be driven out by the mercury, and will escape in a rapid stream of bubbles through the mercury in *G*. By raising *D* the mercury in *A* is brought to the point *q*. When no more bubbles escape at *c*, *D* is brought into its lowest position, as shown in Fig. 114. The mercury in *A* sinks rapidly, and bubbles of air enter from *a* and rise through *A*. When the mercury in *ag* has sunk below the point *a*, the air in *B* is expanded to the volume $A + B$.

At the same time the mercury in the vessel *G*, which excludes the outer air, rises slowly in the tube *bc* to a height which corresponds to the difference of pressure. By again raising *D* the air which has passed from *B* into *A* can be driven out at *c*, the opening *a* being meanwhile closed by the mercury rising toward *A*. The pressure in *A* increases, the mercury in *bc* falling rapidly, while that in *as* rises above the level in *A*. It is obvious that the sum of the two columns of mercury in these side barometer tubes is at every moment equal to the difference in pressure between the expanded air in *B* and the atmosphere.

When the level of the mercury in *A* has again reached *q*, the simple operation of raising and lowering *D* is repeated until no air-bubbles, or only insignificant ones, escape. The apparatus may be compared to the piston air-pump, if we consider the barometer *Ag* with the movable vessel *D* as the cylinder, the mercury as the piston, and the two barometers *bc* and *as* as the valves.

In the above manipulation *bc* remains filled after each stroke with air at the pressure of an atmosphere + the small mercury column to be sustained at *c*. This volume of air, which again expands into *A* when the mercury is lowered, constitutes, in a manner, the dead space of the air-pump.

2. By a simple modification of the manipulation, the dead space may also be exhausted, after the exhausting in *B* has gone far enough. To do this, the vessel *D*, at the end of each stroke, is raised so high that the mercury begins to flow from *q* through *b* toward *G*. If the dimensions of the tube *bc* have been rightly chosen, it fills almost instantly with mercury, the air being completely driven out at *c*. If *D* be now brought rapidly into its lowest position, there is formed over the mercury in *A* a Torricellian vacuum with which the receiver communicates as soon as the mercury has sunk below *a*. It is clear that by repeating this last proceeding, the exhaustion in *B* can be carried to any desired limit. At the first stroke thus made bubbles of air are seen to ascend in *A* from *a*. This soon ceases, however, if the pumping be continued. The column of mercury in *bc* now stands at the full barometric height during the whole stroke, and only at the moment that the opening *a* is left free is it possible to discern, from a quick jerk of the mercury in *bc*, that a small amount of air has actually passed from *B* into *A*. This jerk becomes steadily weaker and at last imperceptible.

By being repeatedly driven over at *b* the amount of mercury in *D* would constantly decrease and would soon stop further exhaustion, unless the mercury in *G* were poured back into *D*. Fortunately, however, the apparatus itself relieves the operator of this trouble. If the tube *bc* is only slightly longer than the barometric height, then, when the level in *G* has been somewhat raised by the overflow of the mercury, the difference of level between *G* and *b* will soon become less than the barometric height. Toward the end of the exhausting, a Torricellian vacuum is formed in *A* at the beginning of every stroke, so that if too much mercury has passed over into *G* it now flows back of itself into *A*, and in a short time the level in *G* is again at the barometric height below *b*.

If the air is to be completely driven out of *bc*, the stream of mercury must hold together and form a column which wholly fills the tube. This result is easily obtained by choosing a tube of not more than 2 to 3 mm. internal diameter, and by avoiding irregular or too sharply curved bends. It is also well to have the tube *q* widen conically where it joins the bulb *A*.

It should be noted that after the apparatus has been completely exhausted, the bottle *D* must be brought to its lowest position before admitting air into the receiver. In other words, the mercury in *ag* should stand below the point *a*, for otherwise the air entering at *h* and rushing through *B* and *s* would throw any mercury above *a* with such force into the empty space *A* that the bulb might easily be broken.

It is advisable to fasten the air-pump at the points *a* and *n* by larger metal bands, the space between the band and the glass being filled with plaster of Paris. The remaining parts of the apparatus should be supported by fairly wide metal bands alone, so as to allow for the different expansion of wood and glass.

It is clear from the description that all of the sources of error introduced by glass stopcocks and greased joints are completely avoided, so that if the receiver *B* is tight it is impossible for air to enter the apparatus. And further, in the second manner of operating as just described, the layer of air, which in the beginning lies between the mercury and the glass because of the incomplete contact between the last two, is gradually driven out during the exhaustion, so that if the pumping be carried on long enough, there is no limit to the attainable exhaustion of air. Much more perfect exhaustion than is necessary for the analytical methods to be described may easily be obtained with this pump.

To carry out with the aid of this air-pump the simultaneous determination of carbon, hydrogen, and nitrogen, the author has devised the form of apparatus and pump shown in Fig. 115.

A is a small combustion tube, drawn out at one end to a bayonet and at the other to a narrow tube. *B* is a calcium chloride tube, to the front side of which is fused a small bulb apparatus for holding a few drops of concentrated sulphuric acid. *C* is a soda-lime tube. *D* is the air-pump; its escape tube *a* is bent upward at *c* in the small mercury trough *G*, so that a graduated tube *E* may be brought over its free end. The gases drawn from the apparatus by the pump must then pass into *E* and collect there. The end *c* of the escape tube is fastened into a hollow in the trough by pouring molten sealing-wax around it. The screw-clamp *H* supports the movable tube *F*, which is connected with the trough by the rubber tube *b* wrapped in linen. The apparatus is connected at *d*, *e*, and *f* by pieces of new black rubber tubing supplied with wire ligatures.

The tube *A* is first drawn out at *g* to a thin tube about 7 cm. long. It is then thoroughly dried over

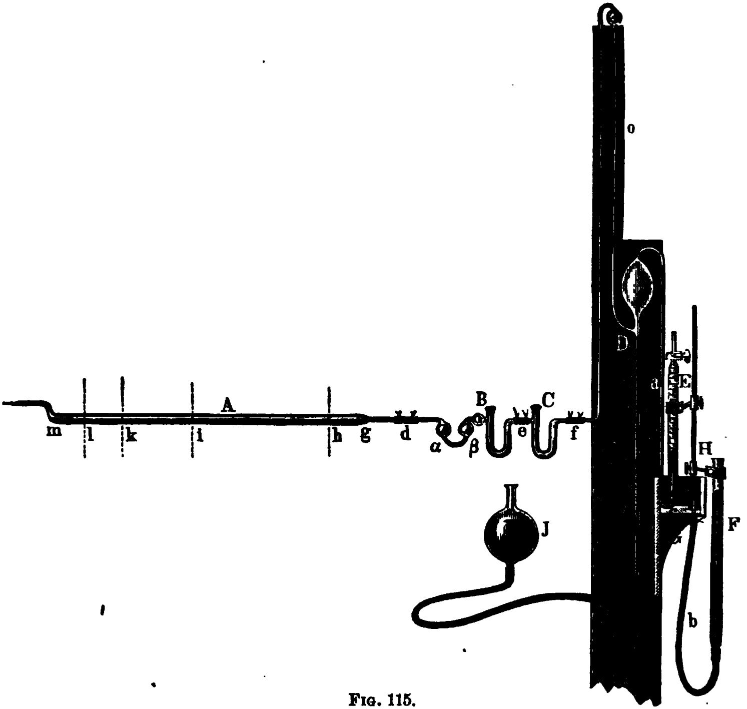

Fig. 115.

a flame, and supplied at *g* with a stopper of ignited long-fiber asbestos. (Short-fiber asbestos might easily be drawn into the calcium chloride tube during the exhaustion.)

The tube is then filled from *g* to *h* — 5 to 8 cm. — with copper powder, from *h* to *i* — 10 to 40 cm., depending on the nature of the substance to be analysed — with granular copper oxide, from *i* to *k* with a mixture of copper oxide and the substance, and from *k* to *l* with pure copper oxide. At *l* a stopper of freshly ignited asbestos is inserted, and a small platinum boat containing about 0.5 g. potassium chlorate is pushed in after it. The tube is now drawn out at *m*, in the blast-lamp flame, to a bayonet, the smallest space possible, about 5 cm., being left between *l* and *m*.

The copper powder and copper oxide are brought close together in the tube, and no canal is left, the combustion gases being thus compelled to move through the whole cross-section of the tube.

To prepare the copper powder, coarse-grained sifted copper oxide placed in a small combustion tube is reduced with hydrogen at low red-heat. The reduced copper is then ignited and allowed to cool in a stream of nitrogen. This latter operation is most simply performed by leading 1 to 1½ liters of dry air over the copper immediately after the reduction, and while the tube is still red-hot; in fact, it is better to raise the temperature somewhat. The oxygen of the air will oxidise the metallic copper lying next the point of entrance, but the length of the layer thus oxidised will be less than 5 cm. If the layer of reduced copper oxide is about 15 cm. long, there is thus obtained for the analysis sufficient copper powder which has been ignited in pure nitrogen. The powder is allowed to cool in a slow current of air, the part of the tube where the air enters being kept red-hot for a short time.

The hydrogen used for the reduction must be freed from arsine, stibine, and hydrocarbons by washing it with a solution of potassium permanganate.

Copper powder thus prepared has a beautiful metallic luster, and repeated experiments have shown that it contains no trace of hydrogen. The formation of carbon monoxide from the carbon dioxide, due to hydrogen in the copper,[1] does not occur here; no water is formed in burning the copper powder to copper oxide. Copper powder made in this manner is an exceptionally good reducing agent, even at a very low red-heat. A close layer 5 to 8 cm. long can with absolute certainty completely decompose, even in a vacuum, the nitric oxide resulting from the combustion of compounds very high in nitrogen. This cannot be done in a vacuum with the ordinary copper spirals.

The grains of sifted copper oxide should be from 1½ to 3 mm. thick. The copper oxide is prepared in the ordinary manner, is freshly ignited before using, and is allowed to cool in a tightly closed pear-shaped flask with narrow neck.

If the substance to be analysed is a solid, it is shaken from a weighing tube into the combustion tube, and is mixed with a copper oxide by means of a bent wire.

To burn liquids of any boiling-point, small bulbs with two capillary side tubes are blown from a thin glass tube (see Fig. 116).

By sucking with the mouth at *c*, there is drawn up into *b* a small amount of an alloy made of 10 parts of Wood's metal (50 parts bismuth, 10 parts cadmium, 27 parts lead, and 13½ parts tin), and 2 to 3 parts mercury. This alloy solidifies at once to a shining and closely adhering thread of metal, without breaking the capillary tube. The melting-point of this alloy lies between 50° and 60° C., quite a little below that of Wood's metal. Moreover, Wood's metal alone breaks the glass walls upon solidifying.

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[1] Schrötter and Lautemann.

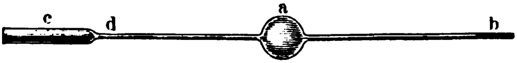

FIG. 116.

When the glass bulb has been thus prepared, the end *c* is cut off at *d*, and the other end is cut off with the nippers until the thread of metal is from 1 to 2 mm. long. The tube is then filled through *d* (Fig. 117) with the liquid to be analysed, the filling being effected by warming and cooling the bulb in the usual manner. The capillary *e* is then melted together at *d*.

The use of a glass bulb of this form admits of exhausting the combustion tube without loss of the substance by evaporation. The bulb can be opened when desired by gently warming the end of the capillary containing the alloy. If the substance is very volatile, this capillary is given a length of from 10 to 12 cm., so that when the end is warmed the liquid in the bulb will not be heated to boiling.

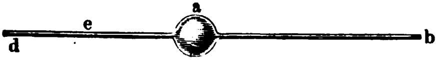

FIG. 117.

The author has found it easily possible with the aid of this bulb to analyse nitrous ether, and can recommend this method of closing the bulb for determinations of vapour density as well as for the ordinary analysis.

In vapour density determinations by Hofmann's method, the metals of Wood's alloy, may be disregarded, for the whole metal stopper weighs only 2 to 3 mg. In combustion analyses the mercury is stopped by the wad of asbestos in the end of the combustion tube, if the heat is not raised unnecessarily high.

A small boat about 3 cm. long, made by bending a piece of platinum foil into the desired form, serves to hold the potassium chlorate. It is convenient to measure off the potassium chlorate in a small glass tube closed at one end; the space occupied by 0.5 g. of the finely pulverised salt is noted by a file mark on the outside of the tube.

The potassium chlorate is heated in the platinum boat until it melts, and after solidifying, and while still hot, it is pushed into the combustion tube.

The bayonet of the tube must be drawn out to a very fine point, so that it may be easily broken off inside a rubber tube slipped over it.

The absorption tubes *B* and *C* (Fig. 115 and Fig. 118) are filled with carefully sifted calcium chloride and soda-lime (size of grains, 1½ to 3 mm.), and are closed at *a* with corks and carefully sealed; small bubbles of air in the sealing-wax may be removed with a hot glass rod. At *b* and *c* (Fig. 118) a little cotton is tightly inserted. These compact stoppers of cotton are sufficiently porous, and the resistance which they offer to the passage of the combustion gases is so great as to render it impossible for the gases to pass through the apparatus too rapidly, and thus escape complete absorption. The U-tubes should be quite small — 20 ccm. capacity for each tube is sufficient — and the sulphuric acid in the bulb tube and the soda-lime should be renewed after each analysis. The calcium chloride may be used many times.

After the apparatus has thus been made ready, and the absorption tubes weighed and carefully connected, the combustion is begun by first placing a support under the calcium chloride tube *B* and bringing it into a horizontal position, as shown in Fig. 119. The sulphuric acid in the bulb tube passes into the bulbs *a* and *β*, the air in the combustion tube being thus brought into direct communication with the air-pump. The apparatus is then carefully exhausted. If the capacity of the combustion tube and the absorption apparatus is small in comparison with that of the bulb of the pump, the air may be driven out of the escape tube *a* and the mercury allowed to pass over at the second rising of the mercury reservoir. The bulb of the air-pump should be of about 500 ccm. capacity, although with a little more time the exhaustion may be made equally well with a smaller bulb. The air-pump used by the author in his experiments had a 150 ccm. bulb made from a large pipette.

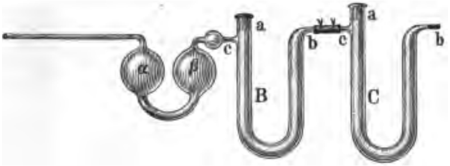

FIG. 118.

Although the tubes are filled with copper oxide, calcium chloride, and soda-lime, the volume of air which they still contain is by no means small. It amounts to from 100 to 150 ccm., as can easily be shown by placing over *c* (Fig. 119) in the mercury trough a measuring tube filled with mercury.

When the air in the apparatus is so rarefied that only very small air-bubbles escape through *a*, the combustion tube is heated to glowing at *l*, and the oxygen of the potassium chlorate is thus set free. The oxygen displaces the air in the apparatus and detaches the layer of air adhering to the large surface of the powdered substances — an operation which many experiments have shown should never be omitted. The apparatus is again exhausted, and when only very small air-bubbles pass over, the copper powder between *g* and *h* is brought to red-heat. The metallic copper unites with the oxygen in the

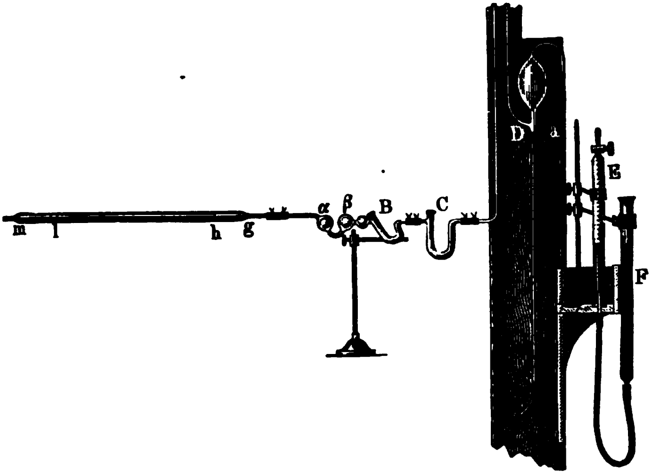

FIG. 119.

tube, so that, by further pumping, the point is soon reached at which only extremely small bubbles escape through *a*. The apparatus is then sufficiently exhausted; the oxygen remaining in the tubes has no effect upon the accuracy of the results.

The calcium chloride tube is now placed upright, and the substance is burned in the usual manner. It is advisable to lay the combustion tube in a trough consisting of several pieces, and to regulate the heat with small asbestos screens. The tubes can be used several times if the heat rises only to a dark red, this sufficing for complete combustion.

The progress of the combustion may be judged by the rapidity with which the gas passes through the sulphuric acid in the drying tube, and by the heating of the soda-lime tube caused by the absorption of the carbon dioxide; not more than half of the soda-lime tube should become warm.

Small amounts of gas take up a great deal of space in chambers which are nearly exhausted, and for this reason the passage of the gas through the sulphuric acid is at first quite violent. For this reason it is advisable and sometimes necessary, if the substance is not explosive, to close the end *c* of the escape tube *a* during the combustion, and to raise the mercury reservoir *J* (Fig. 115) to the height of the bulb of the air-pump. The pump is thus filled with mercury, and the evolved gases soon produce a certain pressure within the combustion tube and the absorption apparatus. The amount of this pressure can be told from the position of the mercury in the tube *o*, and can be regulated by raising or lowering the mercury reservoir.

The end of *c* is closed with a conical glass tube lined with rubber.[1]

The tube is closed at the upper end and fastened into a wooden rod with sealing-wax If this cap be pressed down upon the mouth of *c* by means of a clamp, as shown in Fig. 120, the tube is completely closed.

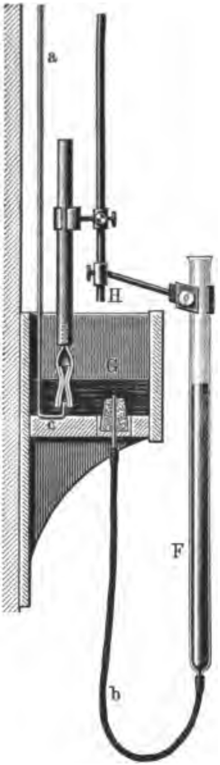

FIG. 120.

When the combustion is ended the cap is removed, and the graduated tube *E* (Fig. 119) is placed over *c*. *E* must always be moistened near the stopcock with a drop of water. The tube *F* which is connected with the mercury trough by the rubber tube *b* is used for filling the graduated tube. A single-bore rubber stopper fitting the graduated tube is fastened into the bottom of the mercury trough (see Fig. 120) with sealing-wax. The rubber tube *b* is fastened to the glass tube which passes through the stopper. If the graduated tube be pressed down firmly over the rubber stopper, it can be easily filled with mercury by raising the tube *F*. And, further, by bringing the tubes *E* and *F* into the position shown in Fig. 119, a gas confined in the measuring tube may be brought under atmospheric pressure and measured, the correction for difference of level of the mercury in tube and trough being thus avoided.

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[1] Bunsen, *Gasometrische Methoden*, 2d ed., p. 161.

Graduated tubes of this form, supplied with a glass stopcock and holding from 75 to 100 ccm., are very convenient for collecting the gas in the Dumas method for determining nitrogen, or in the Schulze determination of nitric acid; they can easily be filled with sodium hydroxide solution by applying suction at the upper end, and the troublesome inverting of the tubes is thus avoided.

After the combustion, the nitrogen in the tube and the absorption apparatus is drawn over into the graduated tube by means of the air-pump. The exhausting is continued until only extremely small bubbles pass over. It denotes no error if later a passage of gas is shown by a periodic movement of the sulphuric acid in the calcium chloride tube, for this is caused by the small quantity of gas which is still in the tubes and which is disregarded in the analyses. It is advisable to exhaust slowly, for the gases need a certain time to move through the capillary spaces in the asbestos and cotton stoppers.

When the exhausting is ended, *E* is placed as in Fig. 119. A thin rubber tube, which is closed in the middle with a screw pinchcock, is slipped over the bayonet, and the point of the latter is broken off inside of the tube. To burn any carbon which may have separated, dry oxygen is led through the tube until the metallic copper begins to oxidise. The carbon dioxide and oxygen are then displaced by air; the current of gas can be regulated as desired by raising or lowering the mercury reservoir of the air-pump.

The apparatus is then disconnected, and after it has assumed the temperature of the balance room, it is weighed. The nitrogen is measured and its weight is calculated, with due allowance for temperature, barometric pressure, and the tension of aqueous vapour.

This method takes about as much time as the Dumas determination of nitrogen. It is especially valuable for the analysis of explosive compounds, for the change in pressure causes a change in the boiling-point. For example, nitro-glycerin can be burned and distilled in a vacuum, without explosion resulting; this cannot be done under ordinary atmospheric pressure.

ANALYSES

Analysis of Aniline

	Found			Calculated
	I	II	III	
	Per cent	Per cent	Per cent	Per cent
Carbon	77.3	77.9	77.4	77.4
Hydrogen	7.6	7.8	8.8[1]	7.5
Nitrogen	14.8	15.0	14.9	15.0
Amount of substance taken	0.2689 g.	0.1154 g.	0.1089 g.	

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[1] Asbestos passed over into the calcium chloride tube.

Analysis of Picric Acid

	Found			Calculated
	I	II	III	
	Per cent	Per cent	Per cent	Per cent
Carbon . .	31.3	31.7	31.1	31.4
Hydrogen . .	2.4[1]	1.6	1.5	1.3
Nitrogen . .	17.9	18.3	18.1	18.3
Amount of substance taken	0.1785 g.	0.164 g.	0.3333 g.	

Analysis of Nitro-glycerin

	Found				Calculated
	I	II	III	IV	
	Per cent	Per cent	Per cent	Per cent	Per cent
Carbon .	15.6	15.7	15.7	16.3	15.8
Hydrogen .	2.6	2.9	2.4	2.3	2.2
Nitrogen .	18.5	18.8	18.9	18.7	18.5
Amount of substance taken	0.144 g.	0.210 g.	0.2803 g.	0.3620 g.	

If, in pumping out the apparatus, the exhaustion is carried equally far both before and after the combustion, the volumes of gas remaining in the tubes must be in both cases the same, and no errors in the analysis would result, provided that these residual gases had within certain limits the same composition. But at the beginning the combustion tube is filled with air, while, after the combustion, it contains a mixture of water vapour, carbon dioxide, and nitrogen, in which the amount of nitrogen is very small in the greater number of cases. For this reason the nitrogen result would be too high if the tube were not filled with oxygen as above described, for there remains after the first exhaustion a certain quantity of air, high in nitrogen, which would be displaced by the gases evolved, while after the combustion a gas mixture low in nitrogen results. Aside from the fact that the greatest vacuum possible may be obtained by filling a space with absorbable gases and then absorbing these gases, the errors which might result from incomplete exhaustion are equalised if oxygen is set free as described; for this oxygen cannot escape from the tube, but on the contrary is taken up by the metallic copper.

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[1] See note, p. 408.

In the analysis of nitro-glycerin the resulting mixture of water vapour, carbon dioxide, and nitrogen contains a large amount of the last-named substance. For this reason the evolution of oxygen may be omitted if the combustion be made in a short tube about 20 cm. long. Moreover, nitro-glycerin does not evaporate to any extent at ordinary temperatures in a vacuum, so that the substance may be weighed in a boat and mixed directly with the copper oxide. A layer of copper powder about 6 cm. long is brought into the combustion tube, then a layer of copper oxide of about the same length, the boat is introduced, the tube filled with copper oxide and drawn out to a bayonet. The tube is then exhausted as completely as possible and is slowly brought to a red-heat, the heating beginning at the metallic copper. The rest of the operation is like that already described.

Even with a pressure of 290 mm. inside the combustion tube, the nitro-glycerin burned without explosion in my analyses.

CHAPTER XII

A CALORIMETRIC METHOD FOR THE DETERMINATION OF THE HEATING POWER OF FUEL

In connection with an extended series of experiments upon the action of furnaces constructed for the smokeless consumption of coal, the author was led to look up the calorimetric determination of the heating power of fuels. An attempt was first made to work with the calorimeter constructed by F. Fischer, but it was soon found that under the given conditions the determinations could not be carried out with this apparatus. In the investigation in question, the coals were in the form of very fine powder resulting from the taking of an average sample from a large amount of coal (see below).

Although many varied experiments were tried, it was impossible to burn the coal so that, excepting the ash, only gaseous products would result: some tar was always formed. The endeavour to obtain a combustion without the formation of tar, by pressing the coal dust into solid pieces (as later described), and by intermixture of indifferent substances, such as infusorial earth, led to no desirable results. Starting with the idea that the preference must be given to that method which would afford a perfectly complete combustion, the author subjected the method of Berthelot[1] to a careful experimental examination, and found that it was actually possible to burn coal with an excess of oxygen and under high pressure, directly to ash, carbon dioxide, water, and nitrogen.

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[1] *Compt. rend.*, **91**, 188.

The combustion was made in an autoclave of such a shape that a beaker could be placed inside of it. Beyond this, the manipulation was the same as that described in detail later. The products of combustion were first passed through a calcium chloride tube, and a Liebig potash bulb with caustic potash tube, then through a red-hot tube containing copper oxide, and again through a calcium chloride tube and a Liebig potash bulb with caustic potash tube.

In all cases there was no trace of tar in the beaker within the autoclave; the coal was burned completely, and the ash was fused to a glassy slag. A Saxon coal was used in the experiments.

1. 0.5 g. of coal burned in an autoclave of 300 ccm. capacity, under a pressure of 6 kg. to the square centimeter, gave 0.0045 g. carbon dioxide and 0.013 g. water in the incompletely burned products of the combustion.

2. 1 g. of coal burned in an autoclave of 300 ccm. capacity, under a pressure of 8 kg. to the square centimeter, gave 0.105 g. carbon dioxide and 0.0086 g. water in the incompletely burned products of the combustion.

3. 0.779 g. of coal was burned in an autoclave of 260 ccm. capacity under a pressure of 16 kg. to the square centimeter. The weight of the last potash bulb was —

Before the experiment, 64.077 g.
After " " 64.077 g.

4. 0.652 g. of coal was burned in an autoclave of 260 ccm. capacity, under a pressure of 12 kg. to the square centimeter. The weight of the last potash bulb was —

Before the experiment, 64.077 g.
After " " 64.076 g.

5. 0.835 g. of coal was burned in an autoclave of 260 ccm. capacity, and under a pressure of 12 kg. to the square centimeter. The weight of the last potash bulb was —

Before the experiment, 64.076 g.
After " " 64.0775 g.

6. 0.9878 g. of coal was burned in an autoclave of 260 ccm. capacity, and under a pressure of 12 kg. to the square centimeter. The weight of the last potash bulb was —

Before the experiment, 64.077 g.
After " " 64.077 g.

These experiments show that in an apparatus of about ¼ liter capacity, 1 g. of coal can be completely burned in an atmosphere of oxygen under a pressure of 12 kg. to the square centimeter.

It cannot be denied that working with a pressure of several atmospheres entails certain inconveniences. Nevertheless, the author is of the opinion that the preference must be given to the Berthelot method above all others, because, on the one hand, the total products of the combustion remain in the calorimeter, thus admitting of a simple and direct measurement of the heat without any calculation, while, on the other hand, complete combustion is attained.

After many unsuccessful experiments the author has finally succeeded in modifying the Berthelot method so that coal in the form of dust can easily be burned, and he has devised an apparatus with which the experiment can be successfully performed with the aid of simple appliances.

The combustion is made in an apparatus similar to that proposed by Berthelot. The coal is pressed into solid pieces in a steel form[1] by means of an ordinary screw-press, is then electrically ignited, and is burned under a pressure of 12 kg. to the square centimeter (11.6 atmospheres).

The object of the technical examination of coal is to determine the average value of a large mass of fuel, so that to obtain accurate results it is necessary that an average sample be selected with great care. To do this a whole car-load of coal is spread out in a flat heap, the coal is taken out in parallel furrows with a shovel. The coal thus obtained, which should amount to several hectoliters, is broken up to the size of hazel nuts with an ordinary hand stamp, again spread out in a flat heap, and coal is taken from as many different places as possible in the heap until 5 kg. is thus obtained. The coal is weighed on an ordinary balance with an exactness of about 1 g. and is then allowed to lie exposed to the air on a large sheet of paper until the difference between two readings made after an interval of about six hours does not amount to more than 20 g. The amount of moisture thus found is termed "mine moisture." The air-dried coal is then ground to a fine powder in a ball-mill. In this way we get a sample which represents sufficiently well the average composition of the coal in question.

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[1] In his calorimetric experiments, Stohmann used solid pieces formed in a similar manner.

Although it is very convenient, for all other analyses, to have the coal in finely pulverised condition, this is quite undesirable in the calorimetric determination. If we attempt to burn coal dust in a current of oxygen, the coal dust lying upon a sheet of asbestos paper, tar is always formed in addition to the gaseous combustion products, if the coal is highly bituminous; in some cases a separation of soot was observed. Moreover, the coal dust cannot be used direct in the Berthelot apparatus, because the combustion is there made in a basket of platinum wire-gauze.

This difficulty can be avoided by exposing the coal dust to high pressure and thus forming it into a small cylinder through which passes a piece of thread for igniting the coal. The arrangement shown in Figs. 121 and 122 is used for this purpose. This consists of a small, four-cornered steel form (Fig. 121), which can be inserted into a small screw-press (Fig. 122). The projections on the side of the block play in slits in the frame of the press.

Through the block of steel is a cylindrical slot which is conically widened at the lower end. In this conical space is inserted the piece *b*, which has the form of a truncated cone. The surface of *b* has on two sides shallow channels in which is laid the piece of thread that is to pass through the coal cylinder when this is made by pressure (see Fig. 121).

The piece of thread should be about 10 cm. long, and after it has been laid along the channels of the bottom piece *b* the latter is inserted into the lower end of the opening of *a*. About 1.2 g. of powdered coal is then shaken into the upper end of the opening, the short steel cylinder *c* is inserted, and the steel plunger *d* is placed in the upper end of the opening. The block is then slid into the press (see Fig. 122), care being taken that the thread does not slip out of position and that it lies in the channels in the steel block, for otherwise it might be cut off when the pressure is applied. This cutting of the thread can be easily avoided by fastening its outer ends into position with small bits of wax. The ends of the thread which have come into contact with the wax can afterward be cut off, and any error which might arise from the presence of particles of wax in the combustible substance can thus be avoided. A piece of thread of a length of 100 mm. weighs only 2½ mg., so that simply measuring the length of the piece employed is sufficient to exactly determine its weight if the weight of a long piece of the thread has previously been determined once and for all.

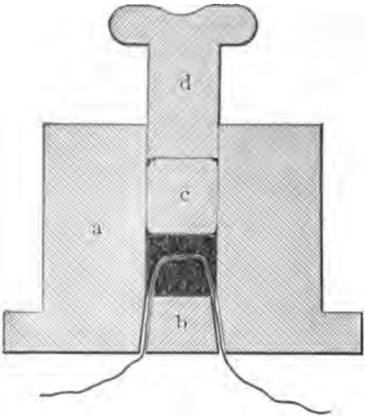


FIG. 121.

The screw of the press is now turned down, and with moderate pressure the coal dust is compressed into a compact, adherent cylinder. The screw is then turned up, the form is withdrawn from the lower guides, the ends of the thread where they have come into contact with the wax are cut off with a knife, and the form is slipped into the upper guides of the press. On again turning down the screw, the coal cylinder is pushed down through the form.

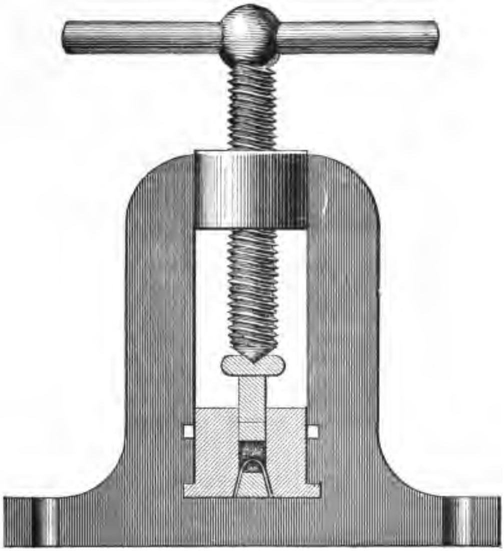


FIG. 122.

The form should be carefully cleaned after use and thoroughly oiled. An excess of oil is removed with filter paper. A trace of oil is intentionally left in the form, since it greatly facilitates the preparation of the coal cylinders.

The coal cylinder thus prepared is freed from adhering coal dust and loose particles of coal by means of a small camel's-hair brush, and the upper part of the cylinder is cut off with a knife until the remaining piece through which the thread passes weighs about 1 g. The sample is then placed upon a watch-glass, covered and accurately weighed.

The combustion is carried out in an autoclave of the form shown in Fig. 123. The autoclave is turned out from a piece of soft cast iron, and is enamelled on the inside. It is unnecessary to use steel, for it is easy to make vessels of cast iron which will withstand a pressure of several hundred atmospheres, even when the walls are no thicker than 5 mm. Moreover, a piece of apparatus made from soft cast iron, if it gives way under high pressure, does not explode but simply cracks open, and the operator is, therefore, not exposed to the possibility of serious injury if the autoclave bursts.

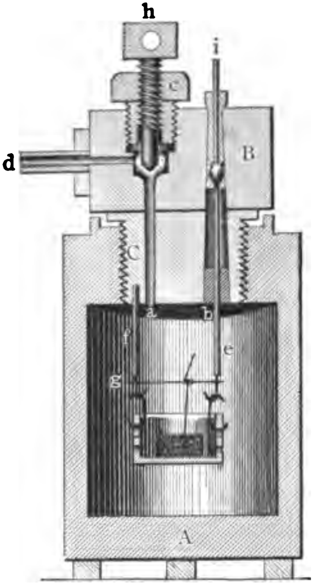


Fig. 123.

The autoclave consists of the vessel *A* and the piece *B* which is screwed into the neck of *A*. The joint is made perfectly tight by means of washers of vulcanite or lead. Two vertical openings *a* and *b* pass through the head *B*. The opening *a* can be closed gas tight by means of the screw valve passing through *c*. Vulcanite is also used as packing for the stuffing box of this valve. Just above the valve seat is a horizontal opening which ends in the tube *d*. The opening *b* is slightly conical in form. Through it passes a metal rod *e* which is slightly widened at one point and is fitted air-tight into the opening by means of a piece of rubber tubing 2½ mm. in internal diameter with a wall 1 mm. thick. *e* is easily inserted in place by first drawing through the conical opening a fairly long piece of rubber tubing by attaching to the end of the tubing a piece of wire, and then shoving the lower end of the rubber tube over *e* until it projects a few centimeters beyond the thickened part of the wire. Upon taking hold of both ends of the rubber tube and stretching it, it is easy to push *e* and the rubber tube into the conical opening to such an extent that tight contact is made at the thickened part of the wire when the rubber is released. When this has been done, the lower end of the tube is drawn down out of the opening and cut off with a sharp knife. The rubber tube then draws back into the opening to such an extent that its end is from 10 to 20 mm. from the mouth of the opening. To completely protect the rubber from the action of the products of combustion, the space between *e* and the sides of the conical opening through the head is tightly packed with long-fibered asbestos. *f* is a thick iron wire fastened into the head *B*. To its lower end and to the lower end of *e* are fastened two pieces of platinum wire about 1 mm. in diameter, and these are connected across directly below the ends of the iron wires by a very fine platinum wire *g*. The lower ends of the two heavy platinum wires are bent upward in the form of hooks, and upon these hooks is suspended by means of two loops of platinum wire a small basket of chamotte.

For the purpose of igniting the coal, a cap is placed over the head of the valve screw *h*, and another one over the upper end of the insulated rod *e* at *i*, and to these caps are fastened brass rods about 15 cm. long. It is well to draw a thin rubber tube over the brass rod which is attached to *i*, so as to completely insulate it. The rods are connected with the poles of a Bunsen dip battery or other source of current by means of ordinary binding clamps and wires.

Before using the bomb the operator should determine the strength of current necessary to bring the thin platinum wire *g* to glowing without melting it. If a dip battery is employed, it is sufficient to simply note the depth to which the plates of the battery must be lowered in order to obtain a current just sufficient to properly heat the wire. The headpiece is, of course, not inserted in place in the bomb when the wire is thus tested.

The thread passing through the coal cylinder is grasped by a small pair of pincers, and the coal is placed in the chamotte basket, the basket itself being suspended on a weighed watch-glass, so that any particles of coal which may be detached from the cylinder will fall upon the glass. The weight of these particles is then determined and subtracted from the weight of the coal cylinder. The headpiece of the bomb is then placed in a support (the ring of a retort stand will answer), and one end of the thread is tied to the thin platinum wire *g*, all other parts of the thread being cut off, and their weight determined by measuring their length.

The autoclave is now closed, care being taken to shake the chamotte basket as little as possible, and to thereby avoid detaching from the cylinder particles of coal which would fall to the bottom of the autoclave and escape combustion.

The headpiece of the autoclave should be tightly screwed into position with the aid of a long-handled wrench, the autoclave being held firmly by placing it in a cylinder shown in Fig. 124. This cylinder is bolted to a table, and has through its bottom three openings, which correspond to three feet projecting from the bottom of the bomb.

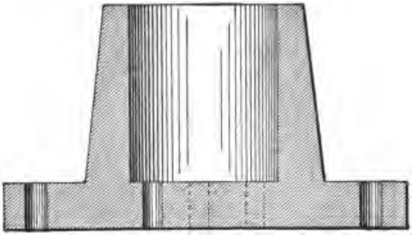


FIG. 124.

When the autoclave has been closed, the tube *d*, projecting from the side of the head, is connected with a branch tube carrying at one end a small manometer *b* (Fig. 125), and joined at the other end to a cylinder containing compressed oxygen.

The valve *o* (Fig. 125) is now opened by giving the spindle half a revolution to the left, and the valve of the oxygen cylinder is then carefully opened and the pressure in the bomb is allowed to rise to about 5 atmospheres. The oxygen cylinder is then closed, and the connection at *d* is slightly opened, so as to allow the gas in the bomb to escape. The larger part of the air originally present in the apparatus is thus removed. The bomb is again tightly connected up at *d*, and the oxygen cylinder opened until the pressure has slowly come up to 15 atmospheres. The cylinder is then shut off, and the valve *o* is closed. The autoclave is disconnected at *d*, and is placed for a moment in a beaker of water, to ascertain whether it is completely tight. If gas bubbles escape from the valve, or around the joint between the headpiece and the body of the bottom, the screws must be turned down tighter until no leakage can be noticed. If this leakage cannot be stopped by tightening the screws, the washers must be renewed, and the face of the valve must be reground.

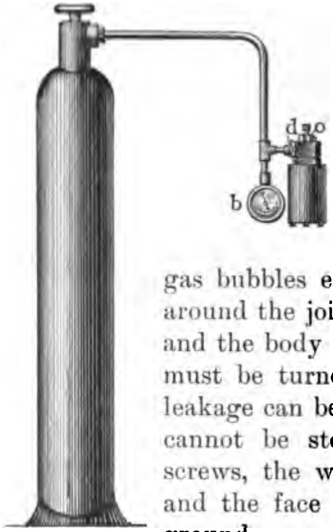


FIG. 125.

If compressed oxygen is not at one's disposal, the autoclave can be filled by means of a retort made from a bent iron tube (see Fig. 126). This tube is filled with 40 g. of a mixture of equal parts of manganese dioxide and potassium chlorate. It is connected with the autoclave in the manner shown in the figure. The two flanges at *a* are fastened together by small bolts, with a lead washer between the flanges. The manometer *b* and autoclave *B* are placed in a cylinder of water, to enable one to see at a glance whether the apparatus is wholly tight. The upper part of the retort *A* is first heated with the full flame of a free-burning Bunsen burner, and this heating is discontinued when the manometer shows a pressure of 1 atmosphere. The hot iron tube still contains heat sufficient to set free enough oxygen to bring the pressure up to 6 atmospheres. By loosening the connection at *a* the pressure is allowed to fall until the manometer stands at zero.

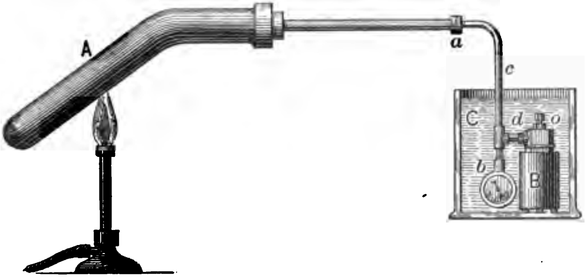


FIG. 126.

Tight connection is then again made, and *A* is carefully heated until the manometer shows a pressure of 12 kg. to the square centimeter. The valve *o* is now closed. *A* is then at once opened, and the autoclave, after being removed from the water, is detached from the manometer at *d*.

It is always possible that in a new apparatus there may be some oil or other organic substance in the retort *A*, and since this would cause an explosion during the generation of the oxygen, it is well to first generate oxygen with *a* open. In one experiment the author purposely added some oil to the mixture of manganese dioxide and potassium chlorate for the purpose of ascertaining the results of such an explosion. It was found that the arrangement of the apparatus above described offered complete protection to the operator. The manometer was broken, but no other damage resulted.

It is self-evident that the mixture of manganese dioxide and potassium chlorate must be completely free from organic substance, sulphur, etc.

The oxygen is given off at temperatures between 210° and 390°; the retort *A* is scarcely attacked at this temperature, and it can be used for hundreds of experiments. The retort is thoroughly cleaned after every determination by boiling it out with water. Direct experiments showed that about 1 ccm. of chlorine is given off with every 1000 ccm. of oxygen. The chlorine is completely removed by inserting into the tube a close roll of brass wire-gauze. The oxygen, which then passes over into the autoclave *c*, is chemically pure. The wire-gauze is renewed after each experiment.

By the foregoing operation the autoclave is filled with oxygen which is almost absolutely pure.

When the autoclave has been filled with oxygen by either of the foregoing methods, it is carefully freed from adhering water by wiping it with filter paper, and is then placed in the calorimeter *G* (Fig. 127), the latter having first been filled with 1 liter of water.

The calorimeter consists of a metal vessel *G* supplied with a cover, and hung in a wooden vessel *H*, a space of about 2 cm. existing between *G* and the wood. In the calorimeter is a stirrer *N*, and a fine thermometer *K*, upon which hundredths of a degree can be read. The stirrer consists of a semicircular piece of sheet-iron, and it can be moved up and down by means of two guide rods and a cord which passes through a hook above.

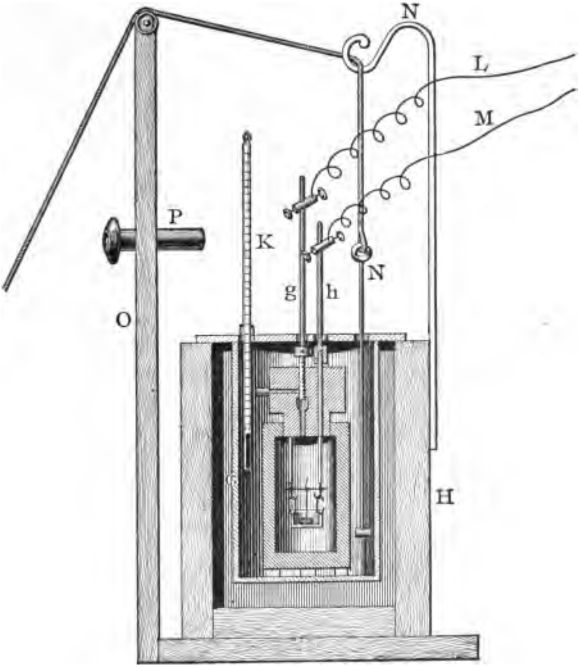


FIG. 127.

The apparatus is connected with a dip-battery by means of the two wires *L* and *M*, and the mercury contacts *g* and *h*. After the autoclave has been placed in the calorimeter and everything made ready, the apparatus is allowed to stand until the thermometer shows no difference in two readings made five minutes apart. The platinum wire in the coal is then heated to glowing by lowering the battery plates, and the ignition of the coal is thus effected. The water is constantly stirred, and the thermometer is watched until the mercury begins to fall again. The temperature at the beginning and the highest temperature at the end are noted.

The calorimétric determination proper takes about fifteen minutes; the complete preparation for it can easily be made in an hour.

The heat-capacity of the whole apparatus (autoclave and calorimeter) is best determined by the combustion of charcoal, cane-sugar, cellulose, or naphthalene. Such an amount of the substance is taken as will give off about the same amount of heat as that produced by 1 g. of average coal.

All errors arising from the radiation of the apparatus, the formation of nitric acid from the nitrogen of the air, etc., are thus made self-compensating in the experiment.

Suitable charcoal is prepared by cutting out small cylinders 1 g. in weight from a piece of ordinary charcoal, placing these pieces in a fire-clay crucible, covering them with charcoal powder, and heating the crucible as high as possible in a gas blast furnace or in a crucible furnace. If the pieces are removed from the crucible while still at a temperature of from 200 to 300°, and are at once transferred to dry weighing tubes provided with tightly fitting ground glass stoppers, the charcoal may then be regarded as consisting of pure carbon exclusive of the ash. The percentage of ash is easily ascertained by burning a few of the pieces in a platinum crucible. The absolute heating power of carbon is 8080 calories, of cane-sugar is 3866, of cellulose 4140, and of naphthalene 9692. If naphthalene is used in calibrating the apparatus, it is compressed into cylinders in exactly the same manner as described above for coal.

Since all coals contain sulphur, some sulphur dioxide and sulphuric acid are always formed in the combustion. Direct experiment showed, however, that an iron apparatus may nevertheless be employed even although it exposes to the action of the gases large surfaces of iron that are not covered with enamel, for it has been found that the amount of heat generated by the action of these acids on the metal of the autoclave is so small that it cannot be measured.

In purely scientific investigations where the price of the apparatus is of secondary importance and where the highest possible accuracy is desired, it is better to use an autoclave that is coated on the inside with platinum.

The following examples serve as illustrations of determinations of this kind:—

1. Coal I.—a mixture of brown coal and bituminous coal. Amount taken, 0.9878 g.

Initial temperature of the calorimeter .	14.19°
Final " " .	18.78°

Hence the combustion caused a rise of temperature of 4.59° in the calorimeter, and 1 g. of coal would have caused a rise of temperature of 4.65°.

2. Coal I. — 0.835 g.

Initial temperature . . .	13.82°
Final " . . .	17.70°
Rise of " . . .	3.88°
" " for 1 g.	4.65°

3. Coal I. — 0.988 g.

Initial temperature . . .	13.68°
Final " . . .	18.29°
Rise of " . . .	4.61°
" " for 1 g.	4.66°

4. Coal II. — 0.952 g.

Initial temperature . . .	14.62°
Final " . . .	18.98°
Rise of " . . .	4.36°
" " for 1 g.	4.47°

5. Coal II. — 0.992 g.

Initial temperature . . .	14.72°
Final " . . .	19.30°
Rise of " . . .	4.58°
" " for 1 g.	4.61°

6. Sugar-coal — 0.5617 g.
Coal I. — 0.1065 g.

Initial temperature . . .	16.22°
Final " . . .	20.09°

Rise of temperature of the calorimeter 3.87°. Since 1 g. of Coal I. gives a rise of temperature of 4.65°, 0.1065 g. will give a rise of 0.49°. Hence the rise of temperature caused by the 0.5617 g. of sugar-coal is 3.38°, and 1 g. of sugar-coal would give 6.01° rise of temperature.

7. Sugar-coal — 0.563 g.
Coal I. — 0.174 g.

Initial temperature . . .	15.84°
Final " . . .	20.02°
Rise of " . . .	4.18°

Rise of temperature from 0.174 g. of Coal I. is 0.81°. Hence 0.563 g. of sugar-coal causes a rise of 3.37°, and 1 g. of sugar-coal would cause a rise of temperature of 6.00°.

The elementary analysis of the sugar-coal gave —

99.5 per cent	carbon
0.1 "	hydrogen
0.3 "	ash.

If the calorific value of the sugar-coal be taken as 99.5 per cent that of pure carbon, the rise of temperature which 1 g. of chemically pure carbon will produce in the apparatus is found by the proportion —

$$99.5 : 100 = 6.01 : x,$$
$$x = 6.04°.$$

Since the absolute heating power of carbon is 8080, the heating power of Coal I. is given by the proportion —

$$6.04 : 4.65 = 8080 : x,$$
$$x = 6220 \text{ calories.}$$

Coal II. —

$$6.04 : 4.54 = 8080 : x,$$
$$x = 6072 \text{ calories.}$$

In the practical using of coal the combustion does not take place in closed chambers, — *i.e.* under constant volume, — but under constant pressure, so that, strictly speaking, the values thus found must be somewhat modified. If, however, we remember that in the combustion of pure carbon or pure cellulose, in closed chambers, no change of pressure takes place in the calorimeter, it is seen that this correction may be wholly disregarded in the case of the ordinary moist coals.

For Coal I., for example, the recalculation gave a correction of 6.6 calories, a figure which, even in the most accurate scientific researches, falls wholly within the limits of the unavoidable errors; in fact, the latest determinations by Berthelot have given the absolute heating power of amorphous carbon not as 8080, as usually taken, but as 8137.4 calories.

In determining the heating power of coals with this method, the water formed in the combustion, together with the moisture present as water in the coal, escapes in a gaseous condition with the products of combustion. The values obtained by the method are not, therefore, directly comparable for technical purposes. Such comparable values, however, are obtained when the heat of evaporation of the water escaping in the combustion is subtracted from the heating power found. This result is termed the available heating power.

This available heating power may be calculated from the Dulong formula—

$$E = 80.8\,C + 342.3\left(H - \frac{O}{8}\right) + 22.2\,S - 6\,W.$$

E is the available heating power.

C is the amount of carbon in the substance in per cent.

H is the amount of hydrogen in the substance in per cent.
O is the amount of oxygen in the substance in per cent.
S is the amount of sulphur in the substance in per cent.
W is the total per cent of water which results from combustion.

Bunte has shown that the values determined by calorimetric methods vary but slightly from the values calculated from the results of a combustion analysis. The calorimetric determination is greatly to be preferred to the combustion analysis because it is shorter, and because it is easier to obtain correct results by means of it.

The available heating power of the coal may be calculated from the result found with the calorimeter by first recalculating this last figure so that it applies to the coal containing mine moisture, and then subtracting from this last result the value

$$\frac{n}{100} \times 600 = 6\,n,$$

n here indicating the per cent of the total water set free from the coal that still contains the "mine moisture"; 600 is the latent heat of evaporation of water.

For most cases arising in practice it will be sufficient to calculate the average amount of hydrogen contained by the coal in question in the ash-free and water-free condition, to then add to that the water found on drying at 120° C. and the "mine moisture," and to multiply the sum of these three percentage values by 6 and then to subtract this amount from the absolute heating power.

If an analysis of the coal has not been made, the following average values for the hydrogen present may be used: —

Bohemian and similar brown coals .	6.0 per cent
Bituminous coal	5.5 " "
Anthracite coal	4.0 " "

More exact figures are obtained by directly determining the amount of water formed in the combustion. This can be done by weighing the autoclave before filling it with oxygen and weighing it again after combustion has taken place and the gaseous products of combustion have been removed, and determining by titration the sulphuric acid and nitric acid which have been formed in the combustion. The increase of weight of the autoclave after subtraction of the weight of the ash and of the anhydrides of sulphuric and nitric acids gives the amount of water which has been formed.

It is better, however, to make a direct determination of the water by means of combustion analysis, as proposed by F. Fischer. This is done by placing from 0.2 to 0.3 g. of coal in a boat in a combustion tube which contains a layer about 40 cm. long of granular copper oxide, and then burning the coal in a current of oxygen. The water which is set free is absorbed in a calcium chloride tube and weighed. In making the analysis it is advisable to heat about 15 cm. of the copper oxide which lies next to the calcium chloride tube not to glowing, but only to from 200 to 300° C., and to thus avoid the passage into the calcium chloride of any sulphuric acid which is produced by the combustion of the sulphur in the coal. The total amount of sulphur will be retained by the slightly heated copper oxide, while all of the water escapes. A small wash-bottle containing concentrated sulphuric acid is placed behind the calcium chloride tube to enable the operator to judge of the speed of escape of the gases formed in the combustion.

As an illustration of the method of calculation of the available heating power from the analytical results, the following example is given:—

A very good sample of brown coal was analysed. The coal had 7 per cent of "mine moisture." The air-dried coal contained 19.5 per cent of hygroscopic water when dried at 120°, and 3.8 per cent of ash. Its absolute heating power was 5818 calories. The coal contained $100 - (19.5 + 3.8) = 76.7$ per cent of coal substance. If we assume that the coal substance of a first-class brown coal contains 5.8 per cent of hydrogen, then the air-dried coal contained $\frac{76.7 \times 5.8}{100} = 4.45$ per cent of hydrogen, from which, in the combustion, would result $4.45 \times 9 = 40.05$ per cent water. 19.5 per cent of hygroscopic water is, however, already present in the coal, therefore the combustion gases will contain $40.05 + 19.5 = 59.5$ per cent of water, which has $6 \times 59.5 = 357$ calories of latent heat of evaporation. The air-dried coal therefore has an available heating power of $5818 - 357 = 5461$ calories. Since, however, the original coal contained 7 per cent of "mine moisture," the available heating power of the residual 93 per cent of air-dried coal $\frac{5461 \times 93}{100} = 5078.7$ calories. To ascertain the available heating power of the coal containing "mine moisture," the latent heat of evaporation of this "mine moisture," $7 \times 6 = 42$ calories, must be subtracted from the result just obtained. The available heating power of the coal under examination is therefore $5078.7 - 42 = 5036.7$ calories.

CHAPTER XIII

THE DETERMINATION OF THE HEATING POWER OF GASES

THE determination of the heating power of gases can be carried out satisfactorily in the gas calorimeter devised by Junker, provided the operator has at his disposal a large volume of gas which is stored in a gasometer and is therefore not changing in composition during the analysis. With the Junker apparatus, however, it is not possible to determine the heating power of such small volumes of gas as 2 or 3 liters, nor does it enable the operator to follow the frequent changes that occur in the composition of a gas mixture that is being evolved from a gas producer.

The incandescent system of gas lighting which has recently been so widely introduced, depends for its efficiency upon the heating power of the gas, and not upon its luminosity. There is but little doubt, therefore, that the future trend of gas production will be along the lines of such products as water gas or producer gas, and that the chief problem of the manufacture will be to make a cheap gas of high heating power. The manufacture of gas in retorts, so far as illuminating gas is concerned, will also probably be replaced in part by the manufacture in generators. This change will make necessary a much more elaborate chemical control, if the product is to be fairly constant in composition, than has been customary in gas works up to the present time. It is, therefore, highly desirable that the chemist possess a rapid method for determining the heating power of gases.

In connection with another series of investigations the author has devised a calorimetric method which has proven to be very satisfactory. The arrangement of the apparatus is shown in Fig. 128.

It consists essentially of a burner *A*, so constructed as to be supplied on the one side with oxygen and on the other with the gas under examination. It is thus possible to reduce the total amount of the products of combustion to such an extent as to make it possible to completely cool them in the copper tube *B* of a length of only 18 cm. and a width of 3.3 cm. The upper end of the copper tube is closed, and the tube itself is firmly fastened to a tripod support. A glass tube *E*, 34 cm. long and 5 to 6 cm. wide, is placed over *B*, and is held in position by means of a large rubber stopper *d*. During the combustion the water in *E* is vigorously stirred by means of a simple stirrer *F*. The temperature before and after the experiment is measured with an accuracy of about 0.02° with a delicate thermometer *G* graduated in tenths of a degree. The gas under examination is stored in a small flat reservoir *H*, which is of sheet zinc, and is closed above and below by the brass stopcocks *k* and *i*.

The gas is ignited by means of a very small hydrogen flame, the hydrogen being supplied by the gas generator *L*.

It is essential that equal quantities of hydrogen and oxygen be used in the different determinations. The supply of these gases through the two fine capillary tubes *m* and *n* is therefore regulated by opening the stopcocks of the hydrogen generator *L* and the oxygen holder *O* to such an extent that bubbles of gas will just fail to escape from the open ends of the glass tubes dipping down in the cylinders *p* and *q*. In this way it is possible to cause these gases to pass

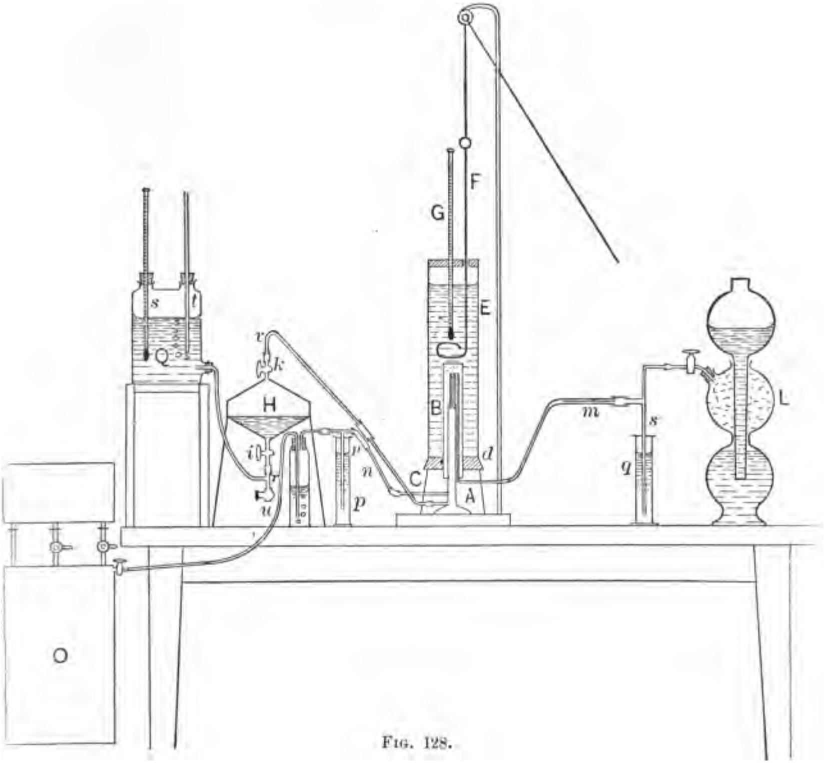


FIG. 128.

through openings of the same size under very nearly the same pressure.

The arrangement of the burner *A* is shown in detail in Fig. 129. A wide brass tube *h* is fastened to an iron base *g*. In the side of *h* there is a small tube *c* for the introduction of the oxygen. To the upper end of the large tube *h* is fastened a porcelain tube *d* which serves to prevent loss of heat by conduction downward through the metal. Inside of the tube *h* are the tube *a* through which is introduced the gas to be burned and a second very small copper tube *b* for the introduction of the hydrogen. Both of these inner tubes terminate in small porcelain tubes.

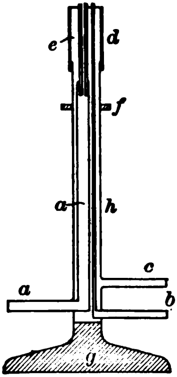


FIG. 129.

To ascertain the heating power of a gas, transfer it to the reservoir *H* in such a manner that it will have a slightly greater pressure than the external atmosphere. After reading the temperature and the height of the barometer, open the stopcock *k* for an instant to bring the gas to atmospheric pressure. Then join the reservoir *H* to a glass T *r*, close the lower end of *r* at *u* with a piece of rubber tubing and a pinchcock, and connect the side arm of *r* with the bottle *Q* by means of a piece of rubber tubing. In one of the necks of *Q* the thermometer *s* is inserted air-tight. With the aid of the glass tube *t* the water can be caused to flow from *Q* at a constant pressure. By opening the pinchcock at *u* for a moment the rubber tube from *Q* can be entirely filled with water.

Fill the calorimeter *E* with 500 ccm. of water and after stirring it thoroughly with the stirrer *F* measure the temperature as accurately as possible with the thermometer *G*. The burner is, of course, not yet placed in position under *B*. When the temperature of the water in *E* has been ascertained, a minute hydrogen flame is lighted in the burner, and a current of oxygen is then turned on. The rapidity of the oxygen supply must be determined once and for all by a few preliminary experiments. The entrance of the oxygen must be so rapid that during the combustion of the gas a glowing splinter will at once burst into flame when brought to the mouth of the copper tube *B*. Now place the calorimeter over the burner, open the stopcocks *k* and *i* of the reservoir *H*, and after a few seconds shut off the stream of hydrogen. The ignition of the gas from *H* is usually accompanied by a faint buzzing sound. If care is taken that the hydrogen flame burns approximately the same length of time in the calorimeter in all experiments, very uniform results are obtained. When the combustion has once been started, the water in the calorimeter is constantly stirred to keep its temperature uniform throughout.

Gas bubbles will be seen rising from the lower end of *t* in the bottle *Q* as long as water flows from the bottle to the reservoir *H*. The end of the experiment is indicated by the appearance of water at *v* in the glass tube which connects the reservoir with the burner. The temperature of the water in *E* is at once read and then the water is stirred until the thermometer begins to sink. The thermometer usually rises a little after the combustion is finished, since the equalization of the heat in the calorimeter takes place only slowly.

The calibration of the apparatus is effected by the combustion of hydrogen. The gas reservoir is filled with hydrogen in the manner above described and this gas is then burned. The rise in temperature of the water thus obtained as compared with the rise in temperature resulting from the combustion of another gas gives us the means of calculating the heating power of the latter.

A series of such determinations follows: —

Contents of gas reservoir *H* 2388 g. at 18.3° C. The small hydrogen igniting flame burned thirty seconds in each case.

Number of Experiment	Thermometer *s* °C.	Barometer mm.	Initial Temperature of Thermometer *G* in Calorimeter *E*. °C.	Final Temperature of Thermometer *G* in Calorimeter *E*. °C.	Rise of Temperature in Calorimeter
1	6.10	755.2	6.50	17.40	10.90
2	6.15	755.2	6.60	17.40	10.80
3	6.25	755.2	6.80	17.65	10.85
4	6.30	755.2	7.00	17.84	10.84
5	7.70	734.0	8.20	18.68	10.48
6	8.50	735.0	8.84	19.36	10.52

The first four determinations were made on the 15th of February, 1900; the last two on the 21st of February, 1900. From the first four determinations there is obtained an average rise of temperature of 10.847° with hydrogen at a temperature of 6.1° and under a barometric pressure of 755.2 mm. The last two determinations give for the same temperature and pressure an average value of 10.83°. The contents of the gas reservoir in hydrogen at 6.1° C. and 755.2 mm. pressure therefore gives an average rise of temperature of 10.838° C. For the sake of illustration the following details concerning the determination of the heating power of a sample of producer gas are given.

Thermometer *s*	12.9°
Barometer	753.2 mm.

Reading on the thermometer *G* in the calorimeter: —

Initial temperature	9.82° C.
Final temperature	14.03° C.
Rise of temperature in calorimeter .	4.21° C.
Duration of ignition flame	30 seconds.

Since the tension of aqueous vapour at 6.1° is 7 mm. and at 12.9° is 11.1 mm., 4.1 mm. must be subtracted from 753.2 mm. in making the calculation. The rise of temperature which the gas under examination would have given if it had been brought into the reservoir at a temperature of 6.1° and a pressure 755.2 mm. is found by the equation: —

$$749.1 : 755.2 = 4.21 : x,$$
$$x = 4.35^\circ \text{ C.}$$

If the absolute heating power of hydrogen given by Favre and Silbermann, viz., 34462 calories, is used, then the absolute heating power of a liter of hydrogen is 3087 calories, since 1 liter of this gas at 0° and 760 mm. pressure weighs 0.089582 g. The heating power of the gas under examination is then calculated according to the following proportion: —

$$10.38 : 4.35 = 3087 : x,$$
$$x = 1239 \text{ calories.}$$

If the gas reservoir is fitted with a correction tube (see p. 61), correction for variation in pressure may be avoided.

The great advantage of the combustion of gases with oxygen lies in the fact that even the slight heating power of gas mixtures which burn only with difficulty can be determined.

The Flame Calorimeter

In controlling the working of an industrial process we may use an empirically graduated instrument that will give the operator an approximate value of the heating power of the gas from the height of the flame which the gas produces when burning. The flame becomes greater as the heating power of the gas increases, the reason for this being that a gas of high heating power naturally needs more oxygen for its combustion, and consequently produces a longer flame than does a gas of lower heating power. The heat necessary to decompose different gases is not constant, and therefore measurements made in this manner are not very accurate.

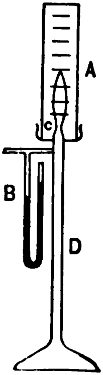


Fig. 130.

The arrangement shown in Fig. 130 will in many cases suffice to determine with sufficient accuracy the heating value of a gas mixture. A burner *c* with a single opening is placed upon a simple stand *D*. The burner is surrounded by a glass cylinder provided with a scale. The pressure under which the gas enters may be read off on the manometer *B*. The instrument is graduated empirically by leading into it gases of known calorimetric value under equal pressures, burning them, and noting the height of the flame in each instance. To determine the heating value of another gas, this is passed into the instrument at the same pressure as was used in the calibration and burned. The height of the flame then gives directly its heating power.

Since the speed of escape of a gas is dependent upon its specific gravity, very light gases will give somewhat too high results, and heavy gases will give values that are too low. Changes in atmospheric pressure will also influence the height of the flame. Notwithstanding these drawbacks it is possible, with the aid of this instrument, to make measurements that will be of considerable value in controlling an industrial process; moreover, such measurements can be made in a few seconds.

CHAPTER XIV

THE DETERMINATION OF SULPHUR IN COAL AND ORGANIC SUBSTANCES

THE sulphur in organic substances may be determined by the method of Berthelot, the compound being burned in an autoclave, and the resulting sulphuric acid being then determined gravimetrically or volumetrically.

If no autoclave is at the chemist's disposal, the combustion may be carried out in an ordinary glass bottle in the manner described below.

The substance under examination is pressed into a small cylinder in exactly the same manner as described for coal in the preceding chapter, a piece of thread being here also pressed into the substance.

If the substance is in liquid form, it may be dropped upon an absorption cube of cellulose through which a piece of thread has been drawn with a needle. These little blocks of cellulose may be obtained from Schleicher and Schüll of Düren, Germany.

The combustion is carried out in a common glass bottle of about 10 liters capacity, Fig. 131. Into the neck of the bottle is inserted a three-hole rubber stopper. Through one opening of the stopper passes a tube with a glass stopcock, the tube being widened above the stopcock into a cylinder containing about 50 ccm. Through the other two openings of the stopper are inserted short glass tubes into which are fused two long platinum wires of about 0.6 mm. diameter. To the lower end of one of these wires is fastened a small platinum basket made by folding together a piece of platinum wire-gauze. This basket hangs about 25 mm. above the bottom of the bottle. The two wires are connected at *c* by a very fine platinum wire.

The glass tubes *b* and *m* are partly filled with mercury for the purpose of easily connecting the two platinum wires with the terminals of an electric battery. When the apparatus is not in use, these two glass tubes are closed with small cork stoppers.

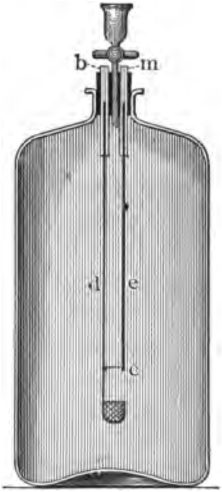


FIG. 131.

To make a determination of sulphur with this apparatus, remove the rubber stopper from the bottle, place the cylinder of the substance under examination in the platinum basket, and twist the thread around the thin wire *c*. Fill the bottle with distilled water, close it with a solid rubber stopper, and place it in an inverted position on an iron tripod which stands in a large porcelain dish. Pour water into the dish until it rises just to the neck of the bottle. Remove the stopper and fill the flask with oxygen in the customary manner. A cylinder of compressed oxygen is very convenient for this purpose. Close the bottle again with the solid stopper and bring it into an upright position. Remove this stopper and lower into the bottle the other stopper carrying the platinum wires and the substance to be burned. Since oxygen is heavier than air, no appreciable amount of it escapes in this operation. A slight excess of pressure is created in the bottle by the combustion and it is therefore best to hold the stopper in place by means of a wire ligature. Now connect the apparatus with the poles of a dip battery or other source of current and ignite the substance by heating the small platinum wire to incandescence. If the substance lies near the bottom of the bottle, the combustion is effected without difficulty, the hot products of the combustion rising to the upper part of the bottle, and fresh oxygen constantly flowing toward the substance. After the combustion is complete pour some cold water over the bottle to cause the pressure within the bottle to fall slightly below that of the external atmosphere, and then introduce into the bottle, through the funnel tube and stopcock, about 100 ccm. of distilled water to which has been added 5 ccm. of concentrated hydrochloric acid and a very small drop of pure bromine.

Since the greater part of the water produced in the combustion remains suspended in the bottle in the form of mist, it is well to allow the bottle to stand for fully an hour, or at any rate until the mist has completely disappeared. All parts of the inner surface of the bottle are then carefully rinsed with the solution which has been introduced and this is poured into a beaker.

In determining the sulphur in coals which necessitate, because of the ash present, a filtration of the hydrochloric acid solution of the sulphuric acid, it is best to wash the bottle, the platinum basket, and the platinum wires with portions of water of 75 ccm. each, and to begin the filtration of the first portion at once. By using these various filtrates for the further rinsing of other parts of the apparatus, it is possible to completely remove all of the sulphuric acid and yet keep the total volume of liquid down to 500 ccm.

The total liquid is now heated to boiling and precipitated in the usual way with barium chloride, the barium sulphate being then filtered off, ignited, purified, and weighed.

The following analytical results illustrate the degree of accuracy which can be obtained by this method.

The analysis of milk casein (prepared by dissolving it three times and precipitating it three times with acetic acid in the cold) gave upon combustion in the bottle two exactly agreeing results of 0.74 per cent sulphur.

According to the determinations of Hammarsten the sulphur contents lie between 0.74 and 0.79 per cent.

The determination of sulphur in different samples of brown coal gave:—

1. By combustion in the bottle 0.74 per cent,
   by Eschke's method 0.66
2. By combustion in the bottle 0.86 per cent,
   by Eschke's method 0.85
3. By combustion in the bottle 0.95 per cent,
   by Eschke's method 0.91

These results show that the variations lie completely within the limits of experimental error, and that the method is thoroughly satisfactory both as to simplicity, rapidity, and accuracy.

CHAPTER XV

THE RECOGNITION AND DETERMINATION OF METHANE BY MEANS OF THE FLAME TEST

On account of the frightful disasters which result almost every year from the explosion of mine gases, it is of the highest importance to be able to detect with absolute certainty the presence of methane in the air of the mine.

Its detection is possible with the aid of the combustion analysis. Samples of the air of the mine are collected for this purpose in small glass tubes provided with stopcocks and containing about 100 ccm. (see p. 8, Fig. 6). The carbon dioxide in these samples is first absorbed and the gas is then burned by one of the methods described on pp. 130 to 143. The volume of carbon dioxide formed in the combustion is equal to the volume of methane which is present in the sample, for methane is almost the only combustible gas which occurs in the air of coal mines. If a burette filled with mercury and provided with temperature and pressure correction is used in making the analysis, it is possible to detect with certainty 0.2 per cent of methane.

Following the suggestion of Davy, it has long been the custom to detect the presence of methane by observing the aureole which the presence of this gas causes to appear around the flame of an oil lamp.

Mallard, Le Chatelier, and Clowes have increased the delicacy of the flame test to about 0.25 per cent by the use of a hydrogen flame. Pieler has obtained the same result with a large lamp fed with alcohol.

Neither of these lamps, however, is suited for general use, for they are either too complex or too expensive.

The author has endeavoured to so modify the mine safety lamp of Friemann and Wolf as to adapt it for the simultaneous detection of methane.

Long experimentation has shown that for this purpose the hydrogen flame is unquestionably superior to all other flames. There is, therefore, attached to the lower part of the lamp a simple apparatus for the generation of hydrogen, with the aid of which a small hydrogen flame can at any moment be started in the interior of the lamp. The hydrogen generator is of sufficient capacity to maintain a flame for from two to three hours.

The lamp (Fig. 132) consists of a benzine burner *A*, a glass cylinder *B*, a chimney *C* made of fine-mesh gauze, the hydrogen generator *D*, and the acid reservoir *E*.

The reservoir of the benzine burner is filled with cotton, and the wick passes up into the tube *a*. This wick can be run up and down by means of a small screw, and if the benzine flame goes out it can be lighted again, without opening the lamp, by the ignitor *b*, which contains bits of phosphorus.

The hydrogen generator *D* is made entirely of lead, and is attached to the lower part of the benzine lamp by means of screws. Short pieces of rubber tubing serve to connect *D* on the one hand with the large reservoir *E*, and on the other with the hydrogen burner *c*. A perforated lead plate *d* serves to support the granulated zinc from which hydrogen is evolved by bringing it into contact with a dilute solution of sulphuric acid (one part of concentrated acid to four parts by volume of water). The flow of acid from the reservoir is regulated by a screw pinchcock *g*, and the size of the hydrogen flame by the other screw pinchcock *e*. The amount of methane in the air of the mine is read off directly on the scale *f*, which is marked upon the side of the glass cylinder *B*. The evolved hydrogen carries with it a fine spray of the acid. To prevent this acid from entering the burner there is introduced, between *i* and the burner *c*, a U-shaped glass tube *h*. The upper part of this tube is loosely filled with cotton. *h* hangs on the outside of the lamp, and it is, therefore, easy to renew the cotton if it should become so moist as to hinder the passage of the hydrogen. The opening of the hydrogen burner is so small as to render it impossible for the flame to

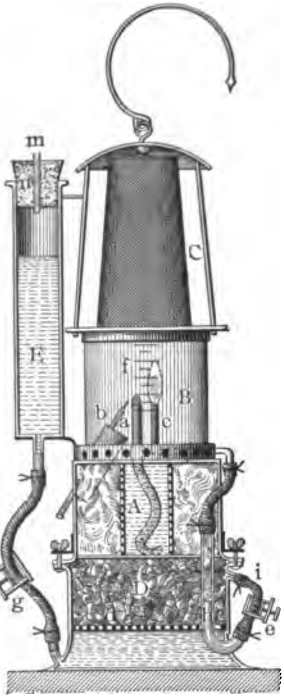


FIG. 182.

strike back into the hydrogen generator, even when this generator is filled with oxyhydrogen gas.

Before going into the mine the generator is freshly filled with zinc and acid, the pinchcock *g* is closed, and the evolution of the hydrogen is started only when the examination of the air in the mine is desired. In testing for the presence of methane, both of the pinchcocks *g* and *e* are opened, and when the hydrogen flame has begun to burn the benzine flame is turned down very low. It is easy to diminish the size of the benzine flame to such an extent as to completely prevent any disturbance by it of the observations. The hydrogen flame is then brought to normal height by means of the pinchcock, and the amount of methane present is read off from the length of the aureole. When the examination is ended, the benzine flame is again turned up high and the pinchcock *e* is closed. The pressure of the hydrogen gas then drives the acid back into the reservoir *E*. Any excess of hydrogen can escape through the capillary tube *m* in the rubber stopper *n*.

CHAPTER XVI

THE GAS LANTERN

An Apparatus for Controlling Gas Processes, and especially for the Inspection of Heating Plants

In many cases the technical chemist is called upon to so conduct a gas process as to cause it to run uniformly over a long period of time. The solution of this problem will be greatly facilitated if there is obtainable a simple,.cheap apparatus which will indicate at once changes in the composition of the gas. This is especially true in the handling of heating plants. In commercial practice, the combustion of coal must be carried on with the aid of air, and a great loss of heat is unavoidable if the introduction of an unnecessary excess of air is not carefully avoided. Such an excess reduces the temperature of the flame, and also carries off a very considerable amount of heat through the chimney. Air contains only 20.92 per cent of oxygen, and, therefore, for every unnecessary volume of oxygen used nearly four times that volume of nitrogen is added.

This explains why the introduction of too much air causes such an enormous loss of heat. Every boiler plant is, of course, provided with a water gauge and pressure gauge, but one rarely finds any arrangement for ascertaining the composition of the flue gas, although this is absolutely essential for economic working. The lack of such an apparatus is doubtless due to the fact that until very recently there was no cheap instrument which equalled the gauge in simplicity, and which at a glance gave information as to the completeness of the combustion at any moment. At the present time a heating plant is controlled either by the use of an apparatus for analysing the flue gases or by the employment of a gas balance. The analysis of the gas takes several minutes, and a gas balance, though it gives the results more quickly, is a very delicate and quite expensive piece of apparatus.

There is described below an arrangement by means of which the condition of the fire or of the process in which gases are being evolved can be judged with ease, this judgment being based upon the fact that a flame changes in size as the amount of oxygen in the gas mixture changes.

The various forms of apparatus proposed by Mallard and others, and described on p. 449, were devised for the purpose of detecting the smallest possible quantities of methane. The apparatus described in this chapter enables us to use a flame for the determination of large amounts of the gases which are mixed with the air. It was found upon experiment that every flame at once changes its form when the composition of the surrounding atmosphere changes. If the flue gases from the furnace be allowed to escape around a flame, the latter at first lengthens, later loses its luminosity, and finally is extinguished when the amount of oxygen in the gas mixture falls below 12½ per cent. The gases from a properly stoked fire usually contain from 12 to 15 per cent of carbon dioxide. It is therefore apparent that a flame cannot burn in the gases escaping from such a fire. If, however, there can be devised an arrangement by means of which the flue gases from a furnace are mixed with so much air that even with the highest amounts of carbon dioxide which the combustion can produce the flame will not be extinguished, the length of the flame can then be employed to judge of the amount of carbon dioxide present in the flue gas. This same arrangement is possible with other gas processes.

Figure 133 shows a simple apparatus which the author has devised for the above-described determination.

A is a pipe which is introduced into the chimney beyond the damper.

B is a pipe through which the flue gases enter.

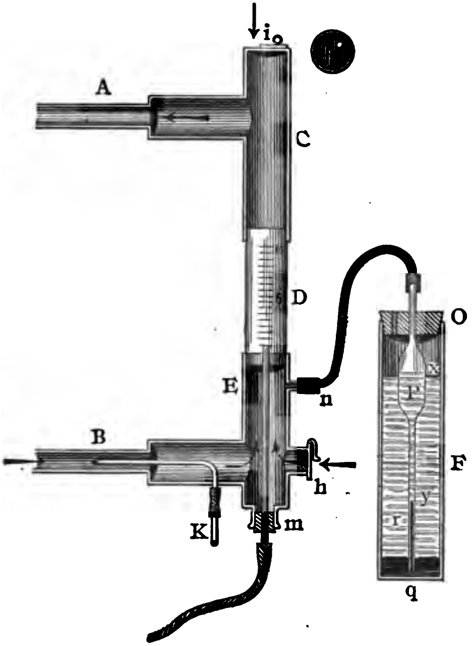
It is advisable to draw off the flue gases at the end of the visible flame, and before they have passed through long stretches of brickwork, because the wall is never air-tight, and large amounts of air are constantly entering through it.

The flame always carries along more or less flue dust. To render it possible to clean out the sampling pipe from time to time, the last portion of it is made about 4 cm. wide, and is so arranged that its outer end can be opened and the whole tube freed from dust by pushing an iron rod through it.

C and *E* are large T-tubes which are joined together by the graduated glass tube *D*.

G is a small tube drawn out to a very small opening at the tip. This tube *G* is connected with the gas supply by the rubber tube *L*, and is held in place in the lower end of *E* by means of the stopper *m*.

Small dampers at *h* and *i* permit of the introduction of any desired amount of air



$\frac{1}{10}$ actual size.

FIG. 138.

A very small lead pipe is connected with *E* at *n*, and this tube is itself joined to the draft measurer *F*. This draft measurer *F* is constructed on the plan suggested by Kretz, and consists of an upright cylinder in which the pipette *P* is held in a vertical position by means of the stopper *O*. This stopper must not fit air-tight in the neck of the cylinder. A mixture *q* of a heavy paraffin oil, containing just enough carbon disulphide to cause it to sink in water, is introduced into the cylinder until it stands at a height of about 4 cm., and this is then covered with a layer of water, as shown in the figure. If the pressure in the pipette *P* diminishes, the water which the pipette contains will rise slightly, while the paraffin oil, which closes the lower end of the pipette, will be drawn up through a much greater distance, the amount of rise depending upon the ratio between the diameter of the pipette at *x* and the diameter of the tube at *y*. The apparatus thus arranged is sufficiently delicate to permit of the reading of the water pressure in hundredths of a millimeter.

In setting the apparatus in operation, the tube *G* is first removed, and the gas entering it through the rubber tube *L* is ignited at the tip of *G*. Ordinary illuminating gas, water gas, or hydrogen may be used for this purpose. A candle or an oil lamp may be used in place of a gas flame, but the apparatus is then much less sensitive.

The dampers *i* and *h* are opened wide, the flame is introduced into the apparatus, and the gas is then regulated so that the flame stands at a certain height. If the draft measurer *F* does not stand in equilibrium when the small dampers are opened, it is brought to this condition by pouring water either into the pipette *P* or into the cylinder of *F*. After adjusting the apparatus, the dampers or draft openings of the furnace are brought into such a position as to cause the production of the maximum amount of carbon dioxide; that is, they are closed as far as possible without causing the extinction of the fire. The small damper *i* is then closed, and the entrance of air through *h* is gradually shut off until the flame just goes out. This position of *h* is then noted, and at the same time a sample of the gas is drawn out through *K* and analysed.

The dampers *i* and *h* are then opened once more, and the combustion in the furnace is brought to normal conditions. The gas issuing from *G* is again ignited, *i* is completely closed, and *h* is closed nearly to the mark. It is now possible to directly observe changes in the height of the flame by reading this off on the scale of the cylinder *D*, the draft measurer being always kept in equilibrium by partially opening and closing the damper *i*. With the aid of the analysis of the samples of gas drawn off through *K* it is easy to ascertain the amounts of carbon dioxide which correspond to the different heights of the flame.

The use of the apparatus above described is by no means limited to the control of heating plants. On the contrary, if made of suitable material, it may be employed in the examination of the gases coming off from sulphate furnaces, chlorine generators, sulphur burners, etc., since all of these gases influence the height of a gas flame or the flame of a lamp. The apparatus is very simple and can easily be constructed. It possesses further the great advantage of being usable in a dark room. When gas flames are employed, they increase in length as the non-combustible constituents of the gas mixture increase in quantity; but with candles and lamps exactly the opposite is true, for here the flame will produce less heat under these conditions, will consequently gasify less combustible material, and the flame will therefore be smaller.

Long experience in the use of this apparatus in the heating plant of the Dresden laboratory has shown that gas flames are best for this purpose. The flame fed with hydrogen is much more sensitive than one supplied with ordinary illuminating gas.

CHAPTER XVII

THE VOLUMETRIC DETERMINATION OF CARBON IN IRON

In connection with a comparative examination[1] of the various methods which have been proposed for the determination of carbon in iron, the author has devised a procedure for volumetrically determining the carbon present.

When iron which contains carbon is dissolved in acids, copper sulphate, or a mixture of chromic or sulphuric acids, a part of the carbon is always set free in the form of hydrocarbons. The author has found, however, that if iron be treated with chromic acid and sulphuric acid in the presence of mercury, it is possible to so conduct the process of solution that no trace of hydrocarbon will form, the total amount of the carbon, on the contrary, being set free in the form of carbon dioxide.

The method is briefly as follows: about 0.5 g. of iron with about 2.3 g. of metallic mercury is dissolved under diminished pressure in a mixture of chromic acid, sulphuric acid, and water. The mixture of air, carbon dioxide, and oxygen — the last gas being set free when the chromic acid is boiled with sulphuric acid — is then measured, and the carbon dioxide is volumetrically determined by absorption with caustic potash.

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[1] *Verhandlungen des Vereins zur Beförderung des Gewerbefleisses.*

The determination is carried out either in the apparatus shown in Fig. 42, on p. 75, or that illustrated in Fig. 110, on p. 380.

The solutions which are used are prepared as follows: —

1. *Chromic Acid*

The manufacturers of chromic acid are in the habit of covering with paraffin the glass stoppers of the bottles in which this preparation is shipped, and consequently it is always possible that organic substances may be present in the acid. It is therefore best for the chemist to prepare the chromic acid himself.

This is done by dissolving 300 g. of commercial potassium dichromate in 500 ccm. of water and 420 ccm. of concentrated sulphuric acid with the aid of heat. When solution is complete, the liquid is allowed to stand for twelve hours, and the clear solution is then decanted from the crystals of primary potassium sulphate which have separated in the meantime. The crystals are washed with from 10 to 12 ccm. of water, and this water is added to the solution. The solution is now warmed to from 80° to 90°, and 150 ccm. of concentrated sulphuric acid is then added, together with sufficient water to keep in solution any chromic acid that may have separated. The whole is now evaporated until a crystalline crust forms, and, after standing for twelve hours, the separated chromic acid is removed by filtration on a platinum cone with the aid of suction.

The mother liquor is again evaporated until a crust appears, and is allowed to stand until a second crystallisation takes place. The liquid should not be too strongly heated during the evaporation, since oxygen might be set free and chromic sulphate be formed. The entrance of any dust must, of course, be carefully avoided.

The chromic acid thus prepared naturally contains some free sulphuric acid and a little primary potassium sulphate. 100 g. of it is dissolved in 300 g. of water and 30 g. of sulphuric acid of 1.704 specific gravity (see below).

The specific gravity of the solution thus prepared should be 1.2. If it is above this figure it contains too much chromic acid, and may give rise to an inconvenient evolution of oxygen when the iron is dissolved.

2. *Sulphuric Acid*

The specific gravity of the acid should be 1.704 at 16 C., corresponding to about 78 per cent of H_2SO_4.

This is prepared by mixing 1000 ccm. of the most concentrated sulphuric acid (this need not be chemically pure) with 500 ccm. of water and 10 g. CrO_3.

This mixture is heated to boiling in a large flask on a sand bath for an hour; the flame is then removed, and air is blown through the liquid for five minutes, with the aid of a blast to remove any carbon dioxide which may have been formed. This long boiling of the acid will, of course, concentrate it to an appreciable degree. It is brought back afterward to the proper concentration by dilution with absolutely pure water. A variation of from 1 to 2 per cent is without result upon the analysis.

MANIPULATION OF THE APPARATUS

About 0.5 g. of the iron to be analysed is placed in a weighing tube (Fig. 134), and the tube is then accurately weighed. The contents is then shaken into the flask of the evolution apparatus, shown in Fig. 110, p. 380, and the weighing tube is then weighed again, the difference between these two weights giving the amount of the sample used.

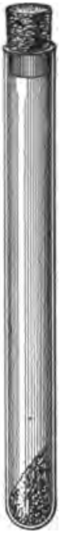

FIG. 134.

About 2.3 g. of mercury is then introduced into the flask by means of a small pipette made from a glass tube (Fig. 135).

The apparatus is now connected together in the manner shown in Fig. 110, and after the measuring tube has been completely filled with mercury, *f* is closed, and the flask is exhausted as completely as is possible by an ordinary water suction pump attached to *k*. To insure the ground-glass joints of the apparatus being air-tight, a little water is placed in the bell *l*, and 30 ccm. of the chromic acid solution is placed in *m*. The stopcock *n* is then closed, and the tube *o* is carefully raised to allow the 30 ccm. of the chromic acid solution to enter the flask. Water is started through the Liebig condenser, and the contents of the flask is heated to the

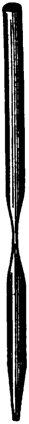

FIG. 135.

boiling-point by means of a very small flame. The boiling proceeds quietly because of the diminished pressure prevailing in the flask, and is continued for thirty minutes. At the expiration of this interval 120 ccm. of sulphuric acid, solution 2, is introduced through the tube *m*, and the contents of the flask is again boiled for thirty minutes.

The pinchcock *f* is not opened until there has been developed in the flask sufficient carbon dioxide to overcome the diminished pressure which first prevailed there, and to thus prevent the entrance of mercury from the burette into the flask. This equalisation of the pressure usually occurs after the addition of the sulphuric acid solution.

In the beginning of the operation carbon dioxide alone is evolved; but as the temperature rises a quite active evolution of oxygen, due to the action of the sulphuric acid on the chromic acid, takes place toward the end of the process.

The possibility that the apparatus may break at any time, and that serious injury to the operator may be caused by the boiling sulphuric acid, should always be borne in mind, and the eyes should always be protected by goggles.

After the second boiling for thirty minutes is finished the flame is removed, and the tube *m* is filled with distilled water. The tube *o* is now very carefully lifted, and there is allowed to enter the flask water sufficient to drive all of the gas over into the measuring tube. Great care should, however, be taken to avoid the entrance of any liquid into the burette. If a burette of the form shown in Fig. 36, II, has been employed, and the gas which has been evolved is not sufficient to fill it down to the graduated portion, then air is admitted until the mercury has fallen to the graduation. The total volume of gas is now measured.

To absorb the carbon dioxide, the burette is connected with a simple gas pipette for solid and liquid reagents, Fig. 32, p. 49, the pipette being filled with a solution of potassium hydroxide. The gas is driven over into the pipette, is drawn back, and is again measured. The difference between the two measurements gives the volume of carbon dioxide which has been evolved.

Several experiments showed that a single passage of the gas mixture into the gas pipette sufficed to remove the last trace of carbon dioxide.

The iron used in the analysis should not be in too large pieces. In the case of steel or gray pig-iron, ordinary borings may be directly employed. With spiegeleisen the pieces must be pulverised in a heavy mortar until they will pass through a sieve of from 400 to 500 meshes per square centimeter.

ANALYTICAL RESULTS

The following analyses will give an idea of the accuracy of the method : —

1. *Gray Cast-iron*

0.5045 g. of iron from the surface of a piece of gray cast-iron gave 32.0 ccm. of carbon dioxide, corresponding to 3.40 per cent of carbon.

The gas residue which was not absorbable by caustic potash was burned with the addition of hydrogen, but gave no trace of carbon dioxide.

0.4797 g. of iron from the inside of the same piece of gray cast-iron gave 28.66 ccm. of CO_2, corresponding to 3.21 per cent C.

0.3889 g. of iron from the inside of the same sample gave 23.45 ccm. CO_2, corresponding to 3.237 per cent C.

0.4260 g. of iron from the inside of the same sample gave 25.85 ccm. CO_2, corresponding to 3.257 per cent C.

2. *Spiegeleisen*

0.2812 g. of spiegeleisen, pulverised until all of the grains passed through a sieve of from 400 to 500 meshes per square centimeter, gave 25.16 ccm. CO_2, corresponding to 4.798 per cent C.

The gas residue, which was not absorbable by potassium hydroxide when burned with hydrogen, gave 0.2 ccm. carbon dioxide, resulting from the hydrocarbons, which had been evolved.

0.338 g. of the same spiegeleisen gave 32.37 ccm. CO_2, corresponding to 5.131 per cent C.

The gas residue, which was not absorbable by potassium hydroxide, was burned with hydrogen, and yielded 0.1 ccm. carbon dioxide, resulting from the hydrocarbons, which had been evolved.

3. *Cast-steel*

0.7932 g. of cast steel gave 13.73 ccm. CO_2, corresponding to 0.9282 per cent C.

Upon passing the gas a second time into the caustic potash pipette, a further contraction of 0.1 ccm. took place.

0.5730 g. of the same sample of cast-steel gave 9.82 ccm. CO_2, corresponding to 0.919 per cent C.

Upon passing the gas a second time into the caustic potash pipette, a further contraction of 0.1 to 0.2 ccm. took place.

0.5900 g. of the same sample of cast-steel gave 10.42 ccm. CO_2, corresponding to 0.947 per cent C.

0.4945 g. of the same sample of cast-steel gave 8.719 ccm. CO_2, corresponding to 0.9455 per cent C.

0.58725 g. of the same sample of cast-steel gave 10.12 ccm. CO_2, corresponding to 0.9240 per cent C.

0.605 g. of the same sample of cast-steel gave 10.52 ccm. CO_2, corresponding to 0.9326 per cent C.

4. *Ingot Iron*

0.5292 g. of ingot iron gave 1.502 ccm. CO_2, corresponding to 0.1523 per cent C.

The gas residue amounted to 30.90 ccm. To this 12.7 ccm. of hydrogen was added, and the mixture was exploded. The volume after explosion was 23.3 ccm., and after passage into the caustic potash pipette was 23.2 ccm., hence no hydrocarbons had evolved.

It is apparent that measurement of carbon dioxide may easily give lower results than weighing of the gas. There are, therefore, added below two analyses of ingot steel, in which a large quantity of steel was dissolved exactly in the method above described, with the aid of mercury, chromic acid, and sulphuric acid, but in which the carbon dioxide instead of being measured was weighed.

2.5155 g. of ingot steel gave 0.098 g. CO_2, corresponding to 1.06 per cent C.

2.5173 g. of ingot steel gave 0.0928 g. CO_2, corresponding to 0.95 per cent C.

Attention must be called to the fact that certain kinds of iron, as, for example, spiegeleisen, are dissolved only with difficulty by a mixture of chromic acid and sulphuric acid. In such a case it is better to use the Berzelius-Wöhler chlorine method, for this can be employed without carefully pulverising the sample.

It is, of course, possible to use in this method any suitable measuring apparatus instead of the burette described; for example, an ordinary gas burette or a nitrometer, if the operator wishes to avoid the expense of a new apparatus and has any measuring instrument at hand. It is also always possible to determine the carbon dioxide by weighing, and to thus completely dispense with the measuring apparatus; but in this case it is necessary to use large amounts of substance, for the weighing of the gas in as large vessels as the ordinary potash pipettes is by no means as delicate and accurate a procedure as the measurement of the volume of the gas.

CHAPTER XVIII

THE VOLUMETRIC DETERMINATION OF THE STRENGTH OF "CHLORIDE OF LIME," PYROLUSITE, POTASSIUM PERMANGANATE AND HYDROGEN PEROXIDE, AND OF THE AMOUNT OF CARBON DIOXIDE IN SODIUM CARBONATE

G. LUNGE[1] has described methods for the determination of the strength of chloride of lime, pyrolusite, potassium permanganate, and hydrogen peroxide in his volumeter, and his directions are given below.

All of these determinations may be made with ease and accuracy with the apparatus shown in Fig. 41, on p. 73.

CHLORIDE OF LIME

This method is based upon the fact that a hypochlorite, when mixed with hydrogen peroxide, immediately gives up its active oxygen, as does the hydrogen peroxide; and the amount of oxygen set free is always exactly equal to twice the amount of active oxygen present in that substance which is in excess. This is shown by the equation —

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

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[1] *Berichte der deutschen chemischen Gesellschaft*, 1885, 1872; 1886, 868; *Zeitschr. f. angewandte Chemie*, 1890, 6.

It is possible by this method to determine the strength of chloride of lime by the use of an excess of hydrogen peroxide of any unknown strength, and also to determine the strength of hydrogen peroxide by the use of an excess of chloride of lime.

A (turbid) solution of chloride of lime is made in the usual manner by shaking 10 g. of the substance with 250 ccm. of water. 5 ccm. of this solution, corresponding to 0.2 g. of the substance, is then removed with a pipette, and placed in the small bottle *q* of the evolution apparatus (Fig. 41). In the inner tube *o* is placed an excess of hydrogen peroxide. 2 ccm. of the commercial hydrogen peroxide will suffice, for that contains an amount of active oxygen nearly equal to ten times its volume. The amount of hydrogen peroxide need not be accurately measured, and its strength need not be known.

The measuring tube *A* is now filled nearly to its wider portion with mercury, and the evolution bottle is connected with the burette and immersed in a beaker of water. The mercury is brought to the same height in the two arms of the manometer, and the initial volume of gas is now read off on the burette. The bottle *q* is now lifted out from the beaker, and the hydrogen peroxide is caused to mix with the solution of chloride of lime by tipping the bottle. The bottle is then shaken for two minutes, again placed in the beaker of water, and the gas volume in the burette is read once more.

When an excess of hydrogen peroxide acts upon chloride of lime, there is set free a volume of oxygen equal to twice that contained in the chloride of lime. Every two volumes of oxygen correspond to two volumes of active chlorine. Therefore the oxygen which is set free shows directly the amount of active chlorine in the bleaching powder; that is, each cubic centimeter of evolved gas corresponds to a cubic centimeter of a chlorine gas.

If 7.917 g. of bleaching powder is used, and if this is dissolved in 250 ccm. of water, and 5 ccm. of that solution is taken for the determination, then every cubic centimeter of evolved gas corresponds to 2 per cent of chlorine in the substance.

Lunge adds that the hydrogen peroxide, to give accurate results, must not be too concentrated. One ccm. of it should set free not more than 7 ccm. of oxygen when mixed with an excess of chloride of lime. The reading of the evolved gas should be made at once, since hydrogen peroxide will of itself slowly set free small quantities of oxygen.

PYROLUSITE

In the analysis of pyrolusite, the finely powdered substance is placed in the outer space of the small bottle (Fig. 41), and is first shaken with some dilute sulphuric acid for the purpose of decomposing any carbonates which may be present. The necessary amount of hydrogen peroxide is then poured into the inner tube, the bottle is closed, and the connection with the burette and the readings of the initial gas volume are carried out as above described. The bottle is then tipped until the hydrogen peroxide flows out upon the substance, and the contents is shaken until the colour of the residue shows that the pyrolusite has been completely decomposed. In the analysis of Weldon mud the reaction takes place at once.

The reaction proceeds according to the equation: —

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2\,H_2O + O_2,$$

Since only half of the evolved oxygen comes from the pyrolusite, 1 ccm. of the gas corresponds to 0.003897 g. MnO_2. If, therefore, 0.3897 g. of pyrolusite is taken for the analysis, the number of cubic centimeters of evolved oxygen corresponds directly to the per cent of MnO_2 present in the substance.

POTASSIUM PERMANGANATE

The strength of a solution of potassium permanganate is determined by placing in a bottle a measured amount of the potassium permanganate solution, containing quite a little free sulphuric acid, and introducing into the tube *o* an excess of hydrogen peroxide. When these two solutions are brought together, the total active oxygen of the potassium permanganate and an equal volume of oxygen from the hydrogen peroxide are at once set free. The reaction proceeds according to the equation: —

$$5\,H_2O_2 + 2\,KMnO_4 + 3\,H_2SO_4 = 8\,H_2O + K_2SO_4 + 2\,MnSO_4 + 5\,O_2.$$

1 ccm. of oxygen weighs 1.43003 mg., hence every cubic centimeter of the gas measured at 0° and under 760 mm. pressure corresponds to 2.8243 mg. $KMnO_4$, according to the equation: —

$$5\,O : KMnO_4 = 80 : 158 = 1.43003 : x,$$

$$x = 2.8243 \text{ mg. } KMnO_4.$$

If it is desired to set free about 50 ccm. of gas, about 40 ccm. of tenth normal of potassium permanganate solution should be used.

The Determination of Hydrogen Peroxide is carried out in exactly the same manner as described for potassium permanganate, except that in this case an excess of potassium permanganate is employed.

Since 1 ccm. of oxygen weighs 1.43003 mg., 1 ccm. of the gas at 0° and 760 mm. pressure corresponds to 1.5194 mg. of H_2O_2, according to the equation: —

$$O_2 : H_2O_2 = 32 : 34 = 1.43003 : x,$$
$$x = 1.5194 \text{ mg.}$$

If commercial hydrogen peroxide of the strength of about 2 per cent is employed, 3 to 4 ccm. of this solution will evolve about 50 ccm. of gas.

In similar manner, we may determine persulphuric acid, perchromic acid, percarbonic acid, periodic acid, perchloric acid, zinc dust, ferrum reductum, lead dioxide, potassium ferricyanide, etc.

THE DETERMINATION OF BICARBONATE CARBON DIOXIDE IN SODIUM CARBONATE

Lunge has described a very simple apparatus for the determination of the bicarbonate carbon dioxide in sodium carbonate.

A glass tube (Fig. 136), 65 mm. long and 6 mm. internal diameter, is widened at one end and there closed by a ground-glass stopper *a*. To the other end of the tube is fastened a capillary tube *d* 60 mm. long. To the interior end of the stopper *a* is attached a glass rod *b*, about 30 mm. long and fitting rather tightly into the glass tube, but not ground into it. The free space in the tube is thus 35 mm. long and 6 mm. wide. The further end of this space, where the capillary is attached, is closed by a little asbestos or glass-wool. The space holds about 0.850 g. of pulverised sodium bicarbonate, an amount which in good material will set free rather more than 110 ccm. of carbon dioxide at 0° and 760 mm. If this amount is either too large or too small for the measuring apparatus that is employed, the space *c* may be increased in size by cutting off the end of the glass rod *b*, or may be diminished by the introduction of more asbestos or glass-wool. The heating of the tube is effected in an air-bath *e*, made from an iron crucible by boring two holes through its sides. The crucible is covered with an asbestos sheet *f*, through which passes the thermometer *g*. A sheet of asbestos *h* projects downward to the bottom of the flame by which the crucible is heated, and thus protects the measuring apparatus from the heat of the flame. This measuring apparatus is joined to the end of the capillary tube *d*. A Lunge

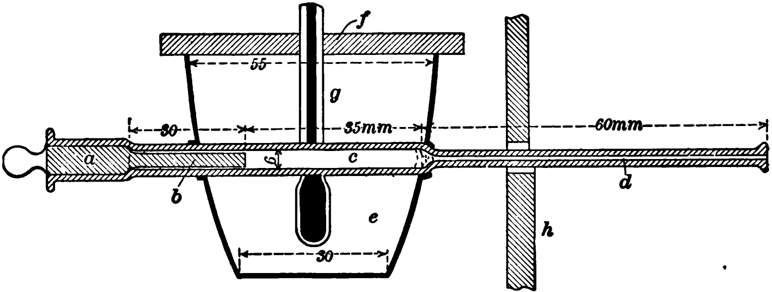

FIG. 136.

gas volumeter or other suitable measuring burette may be employed.

The operation is carried out as follows: the tube is weighed empty and is then filled with bicarbonate, care being taken that no substance remains clinging to the walls of the tube around *a* and *b*. The stopper is then tightly inserted, and the tube is weighed again. It is then placed in the air-bath, in the position shown in the figure, that part of the tube which contains the substance lying wholly within the air-bath. The measuring apparatus is then attached to *d*, the top of the burette is opened, and the air-bath is heated with a fairly large flame until the thermometer stands between 260° and 270°. This usually takes about seven minutes. The heating is then continued for three minutes longer. The stopcock of the measuring tube is then closed, and, after allowing the apparatus to cool for ten minutes, the gas volume is read off.

1 ccm. CO_2 at 760 mm. and $0° = 0.00196633$ g. CO_2 $= 0.0075124$ g. $NaHCO_3$.

In this way the actual amount of bicarbonate present is ascertained. To determine the amount of monocarbonate, the total carbon dioxide is set free by treatment with an acid, and is measured. The difference between the bicarbonate carbon dioxide and the total carbon dioxide gives the carbon dioxide of the monocarbonate. The total carbon dioxide in sodium bicarbonate should amount to at least 50 per cent; theoretically it is 52.38 per cent.

TABLE OF ATOMIC WEIGHTS OF THE ELEMENTS

(F. W. CLARKE)

	H=1		H=1
Aluminum	26.9	Molybdenum	95.3
Antimony	119.5	Neodymium	142.5
Argon	?	Nickel	58.25
Arsenic	74.45	Nitrogen	13.93
Barium	136.4	Osmium	189.6
Bismuth	206.5	Oxygen	15.88
Boron	10.9	Palladium	106.2
Bromine	79.34	Phosphorus	30.75
Cadmium	111.55	Platinum	193.4
Calcium	39.8	Potassium	38.82
Carbon	11.9	Praseodymium	139.4
Cerium	138.0	Rhodium	102.2
Cesium	131.9	Rubidium	84.75
Chlorine	35.18	Ruthenium	100.9
Chromium	51.7	Samarium	149.2
Cobalt	58.55	Scandium	43.8
Columbium	93.0	Selenium	78.6
Copper	63.1	Silicon	28.2
Erbium	164.7	Silver	107.11
Fluorine	18.9	Sodium	22.88
Gadolinium	155.8	Strontium	86.95
Gallium	69.5	Sulphur	31.83
Germanium	71.9	Tantalum	181.5
Glucinum	9.0	Tellurium	126.5
Gold	195.7	Terbium	158.8
Helium	?	Thallium	202.61
Hydrogen	1.000	Thorium	230.8
Indium	113.1	Thulium	169.4
Iodine	125.89	Tin	118.1
Iridium	191.7	Titanium	47.8
Iron	55.6	Tungsten	182.6
Lanthanum	137.6	Uranium	237.8
Lead	205.36	Vanadium	51.0
Lithium	6.97	Ytterbium	171.9
Magnesium	24.1	Yttrium	88.3
Manganese	54.6	Zinc	64.9
Mercury	198.50	Zirconium	89.7

Reduction of a Gas Volume to 0° and 760 mm.

If V is the volume of a gas at $t°$ and h mm. pressure of mercury, then at 0° and 760 mm. pressure the volume

$$V_0 = \frac{V}{1+0.003670\,t}\,\frac{h}{760}.$$

Value of $(1+0.003670\,t)$ for $t = -2$ to $+4°$.

t	$1+0.003670\,t$	$\text{Log}\,\frac{1}{1+0.003670\,t}$	t	$1+0.003670\,t$	$\text{Log}\,\frac{1}{1+0.003670\,t}$
	0,	0,		1,	9, −10
−2°.0	99266	00320	1°.1	00404	99825
−1.9	99303	00304	1.2	00440	99809
−1.8	99339	00288	1.3	00477	99793
−1.7	99376	00272	1.4	00514	99777
−1.6	99413	00256	1.5	00551	99761
−1.5	99449	00240	1.6	00587	99746
−1.4	99486	00224	1.7	00624	99730
−1.3	99523	00208	1.8	00661	99714
−1.2	96560	00192	1.9	00697	99698
−1.1	99596	00176	2.0	00734	99682
−1.0	99633	00160		1,	9, −10
	0,	0,	2.1	00771	99666
−0.9	99670	00144	2.2	00807	99651
−0 8	99706	00128	2.3	00844	99635
−0.7	99743	00112	2.4	00881	99619
−0 6	99780	00096	2.5	00918	99603
−0 5	99816	00080	2.6	00954	99588
−0 4	99853	00064	2.7	00991	99572
−0 3	99890	00048	2.8	01028	99556
−0 2	99927	00032	2.9	01064	99540
−0 1	99963	00016	3.0	01101	99524
0.0	100000	00000		1,	9, −10
	1,	9, −10	3.1	01138	99509
+0 1	00037	99984	3.2	01174	99493
0.2	00073	99968	3.3	01211	99477
0.3	00110	99952	3.4	01248	99461
0 4	00147	99936	3.5	01285	99445
0 5	00184	99920	3.6	01321	99430
0.6	00220	99905	3.7	01358	99414
0.7	00257	99889	3.8	01395	99398
0.8	00294	99873	3.9	01431	99383
0 9	00330	99857	4.0	01468	99367
1.0	00367	99841			

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.003670\,t)$ for $t = 4.1$ to $14.0°$.

t	$1+0.003670\,t$	Log $\frac{1}{1+0.003670\,t}$	t	$1+0.003670\,t$	Log $\frac{1}{1+0.00367\,t}$
	1,	9, —10		1,	9, —10
4°.1	01505	99351	**9°.1**	03340	98573
4.2	01541	99336	**9.2**	03376	98558
4.3	01578	99320	**9.3**	03413	98542
4.4	01615	99304	**9.4**	03450	98527
4.5	01652	99288	**9.5**	03487	98511
4.6	01688	99273	**9.6**	03523	98496
4.7	01725	99257	**9.7**	03560	98481
4.8	01762	99241	**9.8**	03597	98465
4.9	01798	99226	**9.9**	03633	98450
5.0	01835	99210	**10.0**	03670	98435
	1,	9, —10		1,	9, —10
5.1	01872	99195	**10.1**	03707	98420
5.2	01908	99179	**10.2**	03743	98404
5.3	01945	99163	**10.3**	03780	98389
5.4	01982	99148	**10.4**	03817	98373
5.5	02019	99132	**10.5**	03854	98358
5.6	02055	99117	**10.6**	03890	98343
5.7	02092	99101	**10.7**	03927	98327
5.8	02129	99085	**10.8**	03964	98312
5.9	02165	99070	**10.9**	04000	98297
6.0	02202	99054	**11.0**	04037	98281
	1,	9, —10		1,	9, —10
6.1	02239	99038	**11.1**	04074	98266
6.2	02275	99023	**11.2**	04110	98251
6.3	02312	99007	**11.3**	04147	98235
6.4	02349	98992	**11.4**	04184	98220
6.5	02386	98976	**11.5**	04221	98204
6.6	02422	98961	**11.6**	04257	98189
6.7	02459	98945	**11.7**	04294	98174
6.8	02496	98929	**11.8**	04331	98159
6.9	02532	98914	**11.9**	04367	98144
7.0	02569	98899	**12.0**	04404	98128
	1,	9, —10		1,	9, —10
7.1	02606	98883	**12.1**	04441	98113
7.2	02642	98867	**12.2**	04477	98098
7.3	02679	98852	**12.3**	04514	98083
7.4	02716	98836	**12.4**	04551	98067
7.5	02753	98821	**12.5**	04588	98052
7.6	02789	98805	**12.6**	04624	98037
7.7	02826	98790	**12.7**	04661	98022
7.8	02863	98774	**12.8**	04698	98006
7.9	02899	98759	**12.9**	04734	97991
8.0	02936	98743	**13.0**	04771	97976
	1,	9, —10		1,	9, —10
8.1	02973	98728	**13.1**	04808	97961
8.2	03009	98712	**13.2**	04844	97945
8.3	03046	98697	**13.3**	04881	97930
8.4	03083	98681	**13.4**	04918	97915
8.5	03120	98666	**13.5**	04955	97900
8.6	03156	98651	**13.6**	04991	97885
8.7	03193	98635	**13.7**	05028	97869
8.8	03230	98619	**13.8**	05065	97854
8.9	03266	98604	**13.9**	05101	97839
9.0	03303	98589	**14.0**	05138	97824

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.003670\,t)$ for $t = 14.1$ to $24.0°$.

t	$1+0.003670\,t$	$\text{Log}\,\frac{1}{1+0.003670\,t}$	t	$1+0.003670\,t$	$\text{Log}\,\frac{1}{1+0.003670\,t}$
	1,	9, −10		1,	9, −10
14°.1	05175	97809	**19°.1**	07010	97058
14.2	05211	97794	**19.2**	07046	97043
14.3	05248	97779	**19.3**	07083	97028
14.4	05285	97763	**19.4**	07120	97013
14.5	05322	97748	**19.5**	07157	96998
14.6	05358	97733	**19.6**	07193	96983
14.7	05395	97718	**19.7**	07230	96968
14.8	05432	97703	**19.8**	07267	96954
14.9	05468	97688	**19.9**	07303	96939
15.0	05505	97673	**20.0**	07340	96924
	1,	9, −10		1,	9, −10
15.1	05542	97657	**20.1**	07377	96909
15.2	05578	97642	**20.2**	07413	96894
15.3	05615	97627	**20.3**	07450	96879
15.4	05652	97612	**20.4**	07487	96864
15.5	05689	97597	**20.5**	07524	96850
15.6	05725	97582	**20.6**	07560	96835
15.7	05762	97567	**20.7**	07597	96820
15.8	05799	97552	**20.8**	07634	96805
15.9	05835	97537	**20.9**	07670	96791
16.0	05872	97522	**21.0**	07707	96776
	1,	9, −10		1,	9, −10
16.1	05909	97507	**21.1**	07744	96761
16.2	05945	97492	**21.2**	07780	96746
16.3	05982	97477	**21.3**	07817	96731
16.4	06019	97462	**21.4**	07854	96716
16.5	06056	97447	**21.5**	07891	96702
16.6	06092	97432	**21.6**	07927	96687
16.7	06129	97417	**21.7**	07964	96672
16.8	06166	97402	**21.8**	08001	96657
16.9	06202	97387	**21.9**	08037	96643
17.0	06239	97372	**22.0**	08074	96628
	1,	9, −10		1,	9, −10
17.1	06276	97357	**22.1**	08111	96613
17.2	06312	97342	**22.2**	08147	96598
17.3	06349	97327	**22.3**	08184	96584
17.4	06386	97312	**22.4**	08221	96569
17.5	06423	97297	**22.5**	08258	96554
17.6	06459	97282	**22.6**	08294	96539
17.7	06496	97267	**22.7**	08331	96525
17.8	06533	97252	**22.8**	08368	96510
17.9	06569	97237	**22.9**	08404	96495
18.0	06606	97222	**23.0**	08441	96481
	1,	9, −10		1,	9, −10
18.1	06643	97207	**23.1**	08478	96466
18.2	06679	97192	**23.2**	08514	96451
18.3	06716	97177	**23.3**	08551	96437
18.4	06753	97162	**23.4**	08588	96422
18.5	06790	97147	**23.5**	08625	96407
18.6	06826	97132	**23.6**	08661	96393
18.7	06863	97117	**23.7**	08698	96378
18.8	06900	97102	**23.8**	08735	96363
18.9	06936	97088	**23.9**	08771	96349
19.0	06973	97073	**24.0**	08808	96334

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.003670t)$ for $t = 24.1$ to $34.0°$.

t	$1+0.003670t$	Log $\frac{1}{1+0.003670t}$	t	$1+0.003670t$	Log $\frac{1}{1+0.003670t}$
	1,	9, —10		1,	9, —10
24°.1	08845	96319	**29°.1**	10680	95593
24.2	08881	96305	**29.2**	10716	95579
24.3	08918	96290	**29.3**	10753	95565
24.4	08955	96275	**29.4**	10790	95550
24.5	08992	96261	**29.5**	10827	95535
24.6	09028	96246	**29.6**	10863	95521
24.7	09065	96231	**29.7**	10900	95507
24 8	09102	96217	**29.8**	10937	95492
24.9	09138	96202	**29.9**	10973	95478
25.0	09175	96188	**30.0**	11010	95464
	1,	9, —10		1,	9, —10
25.1	09212	96173	**30.1**	11047	95449
25.2	09248	96159	**30.2**	11083	95435
25.3	09285	96144	**30.3**	11120	95421
25.4	09322	96129	**30.4**	11157	95406
25.5	09359	96115	**30.5**	11194	95392
25.6	09395	96100	**30.6**	11230	95378
25.7	09432	96086	**30.7**	11267	95363
25.8	09469	96071	**30.8**	11304	95349
25.9	09505	96057	**30.9**	11340	95335
26.0	09542	96042	**31.0**	11377	95320
	1,	9, —10		1,	9, —10
26.1	09579	96027	**31.1**	11414	95306
26.2	09615	96013	**31.2**	11450	95292
26.3	09652	95998	**31.3**	11487	95278
26.4	09689	95984	**31.4**	11524	95263
26.5	09726	95969	**31.5**	11561	95249
26.6	09762	95955	**31.6**	11597	95235
26.7	09799	95940	**31.7**	11634	95220
26.8	09836	95925	**31.8**	11671	95206
26.9	09872	95901	**31.9**	11707	95192
27.0	09909	95897	**32.0**	11744	95178
	1,	9, —10		1,	9, —10
27.1	09946	95882	**32.1**	11781	95163
27.2	09982	95868	**32.2**	11817	95149
27.3	10019	95853	**32.3**	11854	95135
27.4	10056	95839	**32.4**	11891	95120
27.5	10093	95824	**32.5**	11928	95106
27.6	10129	95810	**32.6**	11964	95092
27.7	10166	95795	**32.7**	12001	95078
27.8	10203	95781	**32.8**	12038	95064
27.9	10239	95767	**32.9**	12074	95049
28.0	10276	95752	**33.0**	12111	95035
	1,	9, —10		1,	9, —10
28.1	10313	95737	**33.1**	12148	95021
28.2	10349	95723	**33.2**	12184	95007
28.3	10386	95709	**33.3**	12221	94993
28.4	10423	95694	**33 4**	12258	94978
28.5	10460	95679	**33.5**	12295	94964
28.6	10496	95665	**33.6**	12331	94950
28.7	10533	95651	**33.7**	12368	94936
28.8	10570	95636	**33.8**	12405	94922
28.9	10606	95622	**33 9**	12441	94907
29.0	10643	95608	**34.0**	12478	94893

Tension of Aqueous Vapour

Expressed in millimeters of mercury at 0°, density of mercury = 13.59593 at latitude 45° and at the sea-level.

Calculated from Regnault's measurements by Broch (*Trav. et Mém. du Bur. intern. des Poids et Mes.* I A. 33, 1881).

t	Tension	t	Tension	t	Tension	t	Tension
	mm.		mm.		mm.		mm.
−2.0	3.9499	2°.6	5.5008	7°.1	7.5171	11°.6	10.1614
−1.9	3.9790	2.7	5.5398	7.2	7.5685	11.7	10.2285
−1.8	4.0082	2.8	5.5790	7.3	7.6202	11.8	10.2960
−1.7	4.0376	2.9	5.6185	7.4	7.6722	11.9	10.3639
−1.6	4.0672	3.0	5.6582	7.5	7.7246	12.0	10.4322
−1.5	4.0970			7.6	7.7772		
−1.4	4.1271	3.1	5.6981	7.7	7.8302	12.1	10.5009
−1.3	4.1574	3.2	5.7383	7.8	7.8834	12.2	10.5700
−1.2	4.1878	3.3	5.7788	7.9	7.9370	12.3	10.6394
−1.1	4.2185	3.4	5.8195	8.0	7.9909	12.4	10.7093
		3.5	5.8605			12.5	10.7796
−1.0	4.2493	3.6	5.9017	8.1	8.0452	12.6	10.8503
−0.9	4.2803	3.7	5.9432	8.2	8.0998	12.7	10.9214
−0.8	4.3116	3.8	5.9850	8.3	8.1547	12.8	10.9928
−0.7	4.3430	3.9	6.0270	8.4	8.2099	12.9	11.0647
−0.6	4.3747	4.0	6.0693	8.5	8.2655	13.0	11.1370
−0.5	4.4065			8.6	8.3214		
−0.4	4.4385	4.1	6.1118	8.7	8.3777	13.1	11.2097
−0.3	4.4708	4.2	6.1546	8.8	8.4342	13.2	11.2829
−0.2	4.5032	4.3	6.1977	8.9	8.4911	13.3	11.3564
−0.1	4.5359	4.4	6.2410	9.0	8.5484	13.4	11.4304
		4.5	6.2846			13.5	11.5048
0.0	4.5687	4.6	6.3285			13.6	11.5797
+0.1	4.6017	4.7	6.3727	9.1	8.6061	13.7	11.6550
0.2	4.6350	4.8	6.4171	9.2	8.6641	13.8	11.7307
0.3	4.6685	4.9	6.4618	9.3	8.7224	13.9	11.8069
9.4	4.7022	5.0	6.5067	9.4	8.7810	14.0	11.8835
0.5	4.7361			9.5	8.8400		
0.6	4.7703			9.6	8.8993		
0.7	4.8047	5.1	6.5519	9.7	8.9589	14.1	11.9605
0.8	4.8393	5.2	6.5974	9.8	9.0189	14.2	12.0380
0.9	4.8741	5.3	6.6432	9.9	9.0792	14.3	12.1159
1.0	4.9091	5.4	6.6893	10.0	9.1398	14.4	12.1943
		5.5	6.7357			14.5	12.2731
1.1	4.9443	5.6	6.7824	10.1	9.2009	14.6	12.3523
1.2	4.9798	5.7	6.8293	10.2	9.2623	14.7	12.4320
1.3	5.0155	5.8	6.8765	10.3	9.3241	14.8	12.5122
1.4	5.0515	5.9	6.9240	10.4	9.3863	14.9	12.5928
1.5	5.0877	6.0	6.9718	10.5	9.4488	15.0	12.6739
1.6	5.1240			10.6	9.5117		
1.7	5.1606	6.1	7.0198	10.7	9.5750	15.1	12.7554
1.8	5.1975	6.2	7.0682	10.8	9.6387	15.2	12.8374
1.9	5.2346	6.3	7.1168	10.9	9.7027	15.3	12.9198
2.0	5.2719	6.4	7.1658	11.0	9.7671	15.4	13.0027
		6.5	7.2150			15.5	13.0861
2.1	5.3094	6.6	7.2646	11.1	9.8318	15.6	13.1700
2.2	5.3472	6.7	7.3145	11.2	9.8969	15.7	13.2543
2.3	5.3852	6.8	7.3647	11.3	9.9624	15.8	13.3392
2.4	5.4235	6.9	7.4152	11.4	10.0283	15.9	13.4245
2.5	5.4620	7.0	7.4660	11.5	10.0946	16.0	13.5103

Tension of Aqueous Vapour — *Continued*

t	Tension	t	Tension	t	Tension	t	Tension
	mm.		mm.		mm.		mm.
16°.1	13.5965	**20°.6**	18.0176	**25°.1**	23.6579	**29°.6**	30.7928
16.2	13.6832	**20.7**	18.1288	**25.2**	23.7991	**29.7**	30.9707
16.3	13.7705	**20.8**	18.2406	**25.3**	23.9411	**29.8**	31.1494
16.4	13.8582	**20.9**	18.3529	**25.4**	24.0838	**29.9**	31.3291
16.5	13.9464	**21.0**	18.4659	**25.5**	24.2272	**30.0**	31.5096
16.6	14.0351			**25.6**	24.3714		
16.7	14.1243	**21.1**	18.5795	**25.7**	24.5164	**30.1**	31.6910
16.8	14.2141	**21.2**	18.6937	**25.8**	24.6620	**30.2**	31.8734
16.9	14.3043	**21.3**	18.8085	**25.9**	24.8084	**30.3**	32.0567
17.0	14.3950	**21.4**	18.9240	**26.0**	24.9556	**30.4**	32.2410
		21.5	19.0400			**30.5**	32.4262
17.1	14.4862	**21.6**	19.1567	**26.1**	25.1035	**30.6**	32.6124
17.2	14.5779	**21.7**	19.2740	**26.2**	25.2523	**30.7**	32.7995
17.3	14.6702	**21.8**	19.3920	**26.3**	25.4018	**30.8**	32.9875
17.4	14.7630	**21.9**	19.5105	**26.4**	25.5521	**30.9**	33.1765
17.5	14.8563	**22.0**	19.6297	**26.5**	25.7032	**31.0**	33.3664
17.6	14.9501			**26.6**	25.8551		
17.7	15.0444	**22.1**	19.7496	**26.7**	26.0077	**31.1**	33.5573
17.8	15.1392	**22.2**	19.8701	**26.8**	26.1612	**31.2**	33.7491
17.9	15.2345	**22.3**	19.9912	**26.9**	26.3155	**31.3**	33.9419
18.0	15.3304	**22.4**	20.1130	**27.0**	26.4705	**31.4**	34.1356
		22.5	20.2355			**31.5**	34.3303
18.1	15.4268	**22.6**	20.3586	**27.1**	26.6263	**31.6**	34.5259
18.2	15.5237	**22.7**	20.4824	**27.2**	26.7830	**31.7**	34.7225
18.3	15.6212	**22.8**	20.6068	**27.3**	26.9405	**31.8**	34.9201
18.4	15.7192	**22.9**	20.7319	**27.4**	27.0987	**31.9**	35.1186
18.5	15.8178	**23.0**	20.8576	**27.5**	27.2578	**32.0**	35.3181
18.6	15.9169			**27.6**	27.4177		
18.7	16.0166	**23.1**	20.9840	**27.7**	27.5784	**32.1**	35.5186
18.8	16.1168	**23.2**	21.1110	**27.8**	27.7399	**32.2**	35.7201
18.9	16.2176	**23.3**	21.2388	**27.9**	27.9023	**32.3**	35.9226
19.0	16.3189	**23.4**	21.3672	**28.0**	28.0654	**32.4**	36.1261
		23.5	21.4964			**32.5**	36.3307
19.1	16.4208	**23.6**	21.6262	**28.1**	28.2294	**32.6**	36.5363
19.2	16.5233	**23.7**	21.7567	**28.2**	28.3942	**32.7**	36.7429
19.3	16.6263	**23.8**	21.8879	**28.3**	28.5599	**32.8**	36.9505
19.4	16.7299	**23.9**	22.0198	**28.4**	28.7265	**32.9**	37.1592
19.5	16.8341	**24.0**	22.1524	**28.5**	28.8939	**33.0**	37.3689
19.6	16.9388			**28.6**	29.0622		
19.7	17.0441	**24.1**	22.2857	**28.7**	29.2313	**33.1**	37.5796
19.8	17.1499	**24.2**	22.4196	**28.8**	29.4013	**33.2**	37.7914
19.9	17.2563	**24.3**	22.5543	**28.9**	29.5722	**33.3**	38.0042
20.0	17.3632	**24.4**	22.6898	**29.0**	29.7439	**33.4**	38.2180
		24.5	22.8259			**33.5**	38.4329
20.1	17.4707	**24.6**	22.9628	**29.1**	29.9165	**33.6**	38.6488
20.2	17.5789	**24.7**	23.1003	**29.2**	30.0900	**33.7**	38.8657
20.3	17.6877	**24.8**	23.2386	**29.3**	30.2644	**33.8**	39.0837
20.4	17.7971	**24.9**	23.3777	**29.4**	30.4396	**33 9**	39.3027
20.5	17.9071	**25.0**	23.5174	**29.5**	30.6157	**34.0**	39.5228

Theoretical Densities of Gases

And weights of one liter of the same at 0° and 760° mm. pressure, for latitude 45° and that of Berlin

Substance	Formula	Density		Weight of 1 liter in grams	
		Hydrogen = 2 (Mol. Wt.)	Air = 1	Latitude 45° at sea-level	In Berlin
Acetylene	C_2H_2	25.947	0.89820	1.16143	1.16219
Allylene	C_3H_4	39.921	1.38194	1.78692	1.78811
Ammonia	NH_3	17.012	0.58890	0.76148	0.76199
Arsine	AsH_3	77.918	2.69728	3.48772	3.49003
Bromine	Br_2	159.538	5.52271	7.14115	7.14588
Butane	C_4H_{10}	57.894	2.00411	2.59142	2.59314
Butylene	C_4H_8	55.894	1.93488	2.50190	2.50355
Carbon dioxide . .	CO_2	43.900	1.51968	1.96503	1.96633
Carbon monoxide .	CO	27.937	0.96709	1.25050	1.25133
Carbon oxysulphide	COS	59.937	2.07483	2.68287	2.68464
Carbonyl chloride .	$COCl_2$	98.689	3.41631	4.41746	4.42039
Chlorine	Cl_2	70.752	2.44921	3.16696	3.16906
Cyanogen	C_2N_2	51.971	1.79907	2.32630	2.32784
Ethane	C_2H_6	29.947	1.03667	1.34047	1.34136
Ethylene	C_2H_4	27.947	0.96744	1.25095	1.25178
Hydriodic acid . .	HI	127.559	4.41570	5.70972	5.71351
Hydrobromic acid .	HBr	80.769	2.79597	3.61534	3.61773
Hydrochloric acid .	HCl	36.376	1.25922	1.62824	1.62932
Hydrofluoric acid . .	HF	19.984	0.69178	0.89451	0.89511
Hydrogen	H_2	2.000	0.069234	0.089523	0.089582
Hydrogen selenide .	H_2Se	80.797	2.79694	3.61659	3.61899
Hydrogen sulphide	H_2S	34.000	1.17697	1.52189	1.52290
Hydrogen telluride	H_2Te	129.960	4.49881	5.81720	5.82105
Methane	CH_4	15.974	0.55297	0.71502	0.71549
Nitric oxide . . .	NO	29.975	1.03764	1.34172	1.34261
Nitrogen	N_2	28.024	0.97010	1.25440	1.25523
Nitrous oxide . .	N_2O	43.987	1.52269	1.96892	1.97023
Oxygen	O_2	31.927	1.10521	1.42908	1.43003
Phosphine	PH_3	33.958	1.17552	1.52001	1.52102
Propane	C_3H_8	43.921	1.52041	1.96597	1.96727
Propylene	C_3H_6	41.921	1.45118	1.87644	1.87769
Silicon tetrafluoride	SiF_4	104.131	3.60469	4.66105	4.66414
Sulphur dioxide .	SO_2	63.927	2.21295	2.86146	2.86336
Water vapour . .	H_2O	17.963	0.62182	0.80405	0.80458
Atmospheric air .	...	...	1.00000	1.293052	1.293909

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